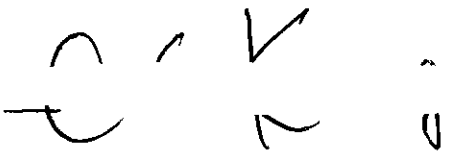
In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institute shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or, in his absence, by the Dean of the Graduate Division when such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.



7/25/68

EQUATION OF STATE
NEAR THE CRITICAL POINT

A THESIS

Presented to

The Faculty of the Graduate Division

by

Kenneth Chia Szu Kiang

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy in the School of Physics

Georgia Institute of Technology

December 1969

EQUATION OF STATE

NEAR THE CRITICAL POINT

Approved:

Chairman

Date approved by Chairman: 1 June 1970

ACKNOWLEDGEMENTS

The author would like to thank his advisor, Dr. H. A. Gersch, for suggesting the present investigation and for his encouragement and advice during the course of it. The helpful comments of Dr. M. Sledd and Dr. J. Ford, who served on the reading committee, are gratefully acknowledge. The author would also like to express his deep appreciation to Dr. and Mrs. V. Crawford for their invaluable counsel and guidance.

The author would also like to thank Mrs. M. Bryant who did a superb job of typing this manuscript.

Finally, the author would like to thank his parents and his wife and daughters for their patience, love and support during this endeavor.

PREFACE

Twenty years ago, as I was boiling water to fix tea for our house guest, I asked my father, "Why does water boil?" My father answered me quickly, "It is a natural phenomenon," and left me wondering in the kitchen. Ten minutes later he came back to me and said, "Son, I really don't know why water boils. Why don't you find out and let me know." And so, I started my career.

In high school, I answered that same question on a test and got an "A" grade. My answer was what I had been told: "Water has a boiling point at $100^{o}C$ and when the temperature reaches the boiling point, water will start to boil." However, in the thermodynamics course at the University, I got an "F" by answering that same question with the same answer I had used in the high school. Because, as the professor said, I did not put "phase transition," "van der Waals' equation of state," "pressure," "volume," ... all the important concepts together to explain this natural phenomenon. In Graduate School, it was all the more fascinating to deal in a microscopic world I had never experienced in my physical life--to rationalize why water can boil.

In the summer of 1966, I attended the Summer Institute for Theoretical Physics on Phase Transitions at Brandeis University. Most of the experts in the field of phase transitions were there and still I discovered this natural phenomenon has not been fully elucidated theoretically. "If I am not wrong, we still do not understand why water can boil!?!" I could not help being upset and so I asked the expert once more.

The expert answered with authoritative gestures and said, "If you want to put it in that way, I must say yes; we do not know why water can boil."

I wrote a long letter to my father and complained about being trapped by the "natural phenomenon." After more than twenty years' research, I had nothing to show--the answer was still, "I do not know." Yet I had received grades for my work in school. And now my future is bound with this problem--for I have no other way with which to make my living.....

One week later, I received my father's letter. The response was, "IT IS A NATURAL PHENOMENON."

OVERTURE

At the age of seventeen, I was a "fresh"-man. Instead of "Geometry," "Algebra," ..., I studied "Philosophy." The definition in the textbook was very clear: Philosophy is the knowledge of Love and and Wisdom. However, no one in the class was satisfied by that clear-cut definition. One of the most striking questions kept bothering us: Why, through thousands of years, have people claimed that the only real knowledge of love and wisdom was their own "Philosophy"? Since then, I have not been "fresh."

Certainly, I shall not have the same attitude toward this thesis for my degree of Doctor of "Philosophy" as others have had for their knowledge of "Philosophy." I feel that I am like a blind man trying to figure out what the monster is standing in front of me. Through more than twenty years of "education" under the "system," I have been told that if I can touch the nose, the body, the teeth, the ears, ... and the tail, I may know it is an elephant. But here is my own question, "Does there really exist an elephant in this physical world?" Under almost seven years of Western education, I have learned the "Faust Spirit," i.e. as long as one keeps digging into the "problem," one should find something. If it is not an elephant, it may very well be "PHYSICS."

C. S. Kiang, Midnight, September 9, 1969
dedicated to those searching
for the truth with LOVE and
WISDOM.

TABLE OF CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Most known substances will undergo at least one phase transition. In many cases the various phases of substances seem quite dissimilar and separate, and transitions between them are abrupt and unheralded. Nevertheless, as one varies, over a suitable range, some external parameter such as the temperature or volume, two different phases can be made more and more similar in their properties until, at a certain critical point, all differences vanish. Beyond this point there only exists one homogeneous equilibrium phase and all changes are continuous and smooth. Perhaps the most well known example of this phenomenon is the transition between the liquid and vapor phases of an ordinary gas at its critical temperature, such as the boiling of water.

It has been discussed, for example, by Uhlenbeck[1] that one requires a theory which can explain general quantitative features of the behaviors of this critical phenomenon. Since the property is common to all substances, one would expect it to be possible to give a very general explanation demanding no exact knowledge of the interaction between molecules. The existence of sharp phase transitions will lead us to believe that the equation of state, mathematically, cannot be represented by one analytical function but consists of several analytically different parts. From the physical point of view, the first attempt at such an explanation was the theory of van der Waals.[2] In this theory the molecules of a substance are

be tested by experiment. Therefore, we are not surprised that considerable attention has been drawn recently to the phenomena which occur very near the critical point. Several recent conferences and many review articles[8] have presented a wealth of new experimental data and theoretical ideas in this area. They have revealed the fact that there are quite marked similarities between apparently very different phase transitions; for example, an antiferromagnet near its Neel point behaves very similarly to a liquid near its critical point, and a superconducting transition is not very different from several ferroelectric transitions. In all cases, there apparently is a general theory for all the phase transitions. To date, experimentally,[8] more precise measurements have been conducted by different techniques such as nuclear magnetic resonance, Mossbauer effect for equilibrium properties and neutron diffraction, ultrasonic attenuation for transport properties near the critical region, and theoretically, the homogeneous argument of the equation of state near the critical point[9] and the use of critical exponents can be considered as the most popular tools for this problem. However, all this simplicity and similarity among phase transitions has not been fully elucidated theoretically. For one thing, there is no equation of state near the critical point derived from a theoretical model which can predict the experimental data, or there is no experimental data available to test the theoretical model (Ising model). (See Reference 8, M. E. Fisher.)

In this thesis, we have presented a homogeneous equation of state near the critical point which is based upon Fisher's liquid droplet model.[10] The expression of the proposed equation of state exactly agrees with the homogeneous argument of the equation of state proposed by Widom

and Griffiths,[9] and depends on only two critical parameters. This model does not provide a calculational scheme for these parameters. However, by use of part of the experimental data to fix these parameters we are able to obtain a striking agreement for all the experimental data near the critical point for most of the substances. An outline of thermodynamics near the critical point which is model independent is given in Chapter II. In Chapter III and IV, we discuss the mechanism of the critical phenomena through the relation between molecular forces and phase transition and the conjunction of cluster theory and condensation. Van der Waals' theory is introduced for long range interaction model and Ising model is considered as a typical short range interaction model. Liquid droplet model is fully discussed in Chapter IV in conjunction with critical phenomena. A general discussion of homogeneous and analytical arguments of equation of state near the critical point is carried on in Chapter V. This is the summary of the works done by Widom, Griffiths and others[9], and possible extensions of their expression for the equation of state near the critical point are included. In Chapter VI, we establish a homogeneous equation of state for liquid droplet model near the critical point[11] and the applications[12] for experimental data also are shown in detail. The significances and future prospects of this research are discussed in the final Chapter.

CHAPTER II

OUTLINE OF THERMODYNAMICS NEAR THE CRITICAL POINT

Thermodynamics is usually subdivided into a theory dealing with equilibirum and into one concerned with irreversible processes. In this chapter we restrict ourselves to the critical behavior of a fluid system based upon the basic postulations of the thermodynamics of phase equilibrium whose logical structure has been constructed by Gibbs and others,[13] and other basic concepts concerning the thermodynamics of critical phenomena.

Basic Postulations

Thermodynamics is a phenomenological theory of matter. It is generally believed that the implications of the first, second and third laws of thermodynamics essentially construct this theory. However, some properties of a material system, such as the existence of an homogeneous phase, validity of the equation of state, etc., require a number of additional assumptions to give a whole description of thermodynamics. The study of the rigorously logical structure of thermodynamics is a master scheme consisting of a number of closely knit deductive systems devised for different types of situations, and itself is a vast area of investigation. Here, we shall not carry on detailed discussion but merely outline the basic postulations concerned with the theory of phase transition, which is entirely based upon the work by Tisza.[14] In this section we shall list the following postulations and briefly discuss the significance of

postulation.

Postulate 1. There exist particular states (called equilibrium states) of simple systems, that macroscopically are characterized completely by the internal energy U, the volume V, and the mole numbers N_1, N_2, . . ., N_n of the chemical components.

Postulate 2. (ENTROPY MAXIMUM PRINCIPLE) There exists a function (called) the entropy S) of the extensive parameters of any composite system, defined for all equilibrium states and having the following property: the values assumed by the extensive parameters in the absence of an internal constraint are those that maximize the entropy over the manifold of constrained equilibrium states.

Postulate 3. The entropy of a composite system is additive over the constituent subsystems. To each simple system the entropy is a continuous homogeneous function with continuous first and piecewise continuous higher derivatives, and is a monotonically increasing function of the energy.

Postulate 4. The entropy of any system vanishes in the state for which

$$\left(\frac{\partial U}{\partial S}\right)_{N_1, N_2, \ldots, N_n, V} = 0$$

In the first postulation we have defined thermodynamic systems and thermodynamic parameters which are measurable macroscopic quantities associated with the system.

Postulate 2 defines the concept of equilibrium, which is one of

the most important concepts in thermodynamics. Since there are no purely observational means for deciding whether an apparently quiescent system has actually reached equilibrium, or is merely stranded in a non-equilibrium state while imperceptibly drifting toward equilibrium, a problem is presented to the experimentalist whether a given system actually is in an equilibrium state, to which thermodynamic analysis may be applied. From postulate 2, we arrive at a theory of normal equilibrium behavior which provides a practical criterion for deciding whether or not equilibrium has been reached.

Several mathematical consequences follow immediately from postulate 3. The monotonic property postulated implies that the partial derivative $(\partial S/\partial U)_{V,N_1,\ldots}$ is a positive quantity, thus the temperature $T = (\partial U/\partial S)_{V,N_1,\ldots}$ (see Section II-2B) is postulated to be non-negative. The continuity and piecewise continuity for higher derivatives imply the possibility for changes of phase.

Postulate 4 is the extension of the third law of thermodynamics. Historically, it was the latest of the postulates to be developed, being inconsistent with classical statistical mechanics and requiring the prior establishment of quantum statistics to be appreciated.

II-2. EQUATION OF STATE

The equation of state is a functional relationship among the thermodynamic parameters for a system in equilibrium.

A. Fundamental relation (fundamental equation)

From postulate 1 and 2, the relation that gives the entropy as a function of the extensive parameters is known as a fundamental relation

treated as mutually attracting elastic spheres. It is assumed that this attractive force between the molecules is for each pair a function of the distance of separation only and is independent of the velocities of other molecules. Due to the recent rigorous study by Kac, Uhlenbeck and Hammer,[3] an infinite long range and weak interaction of the van der Waals' theory is indicated. From these assumptions and together with Maxwell's construction, the van der Waals' theory is able to explain the properties quite well above and below the critical point for some simple substances, and explain, as well, the existence of the critical point. However, this simple physical theory fails to explain the 'anomalies' near the critical point, which was suggested experimentally by the measurement of specific heat in 1964 by A. V. Voronel', V. G. Snigirev, and Yu. R. Chashkin.[4] Furthermore, the equation of state proposed by van der Waals shows disagreement with the experimental data for critical exponents, which is a powerful tool that has been introduced[5] to serve as a common meeting ground between theory and experiment for the critical region. From a mathematical point of view, Yang and Lee[6] have examined the distribution of zeros of the grand partition function and phase transition of a system of molecules with a hard core and finite ranged attractive interaction. A complete description of the equation of state of both the gas and condensed phase can be obtained from the same interaction through the considerations of statistical mechanics. However, the discussion of Yang and Lee does not reveal the detailed nature of the singularities to be expected in any particular type of phase transition and the Ising model (two dimensional) used to demonstrate their theory,[7] so far as I know, can not

or fundamental equation,

$$S = S(U,V,N_1,\ldots,N_n). \tag{2-1}$$

It follows that if the fundamental relation of a particular system is known all conceivable thermodynamic information about the system is ascertainable therefrom. It is an essential feature of the postulations that the fundamental equation and the associated stability considerations can be cast in different forms that depend on the choice of independent variables. As a first step toward developing a systematic transformation theory we solve the fundamental equation for the energy:

$$U = U(S,V,N_1,\ldots,N_n). \tag{2-2}$$

By postulate 3, the entropy is a monotonic increasing function of U, hence, we are permitted to make this transformation.

B. Equation of State

From fundamental equation we compute the first differential

$$dU = (\partial U/\partial S)_{V,N_1,\ldots} dS + (\partial U/\partial V)_{S,N_1,\ldots} dV + \sum_{j=1} (\partial U/\partial N_j)_{S,V,\ldots} dN_j$$

and define the intensive parameters, temperature T, pressure P and chemical potential of the jth component μ_j by

$$T = (\partial U/\partial S)_{V,N_1,\ldots} = T(S,V,N_1,\ldots N_n) \tag{2-3}$$

$$P = -(\partial U/\partial V)_{S,N_1,\ldots} = P(S,V,N_1,\ldots N_n) \tag{2-4}$$

$$\mu_j = (\partial U/\partial N_j)_{S,V,\ldots,N_K} = \mu_j(S,V,N_1,\ldots N_n) \tag{2-5}$$

Such relationships, expressing intensive parameters in terms of the independent extensive parameters are called EQUATIONS OF STATE.

Knowledge of a single equation of state does not constitute complete knowledge of the thermodynamic properties of a system, and knowledge of all the equations of state of a system is equivalent to knowledge of the fundamental equation and consequently is thermodynamically complete.

It is always possible to express internal energy as a function of parameters other than S, V, N. Thus we could eliminate S from $U = U(S,V,N)$ and $T = T(S,V,N)$ to obtain an equation of the form $U = U(T,V,N)$. However, such an equation is not a fundamental relation and does not contain all possible thermodynamic information about the system. In fact, $U = U(T,V,N)$ actually is a partial differential equation. Even if this equation were integrable, it would yield a fundamental equation with undetermined functions. Thus knowledge of the relation $U = U(S,V,N)$ allows one to compute the relation $U = U(T,V,N)$, but knowledge of $U = U(T,V,N)$ does not permit one inversely to compute $U = U(S,V,N)$.

C. Legendre Transformation

In the fundamental relation, the extensive parameters play the roles of mathematically independent variables, whereas the intensive parameters arise as derived concepts. This situation is in direct contrast to the practical situation dictated by convenience in the laboratory. The extreme instance of this situation is provided by the conjugate variables entropy and temperature. The question therefore arises as to the possibility of recasting the mathematical formalism in such a way that intensive parameters will replace extensive parameters as mathematically independent variables. It is well known that such a reforma-

tion is possible through Legendre transformation. (The summary of the formalism for Legendre transformation will be discussed in Appendix A.) Thus we can obtain various other representations for thermodynamic functions. Furthermore, we shall notice that these thermodynamic representations are most commonly used as a meeting ground for theoretical prediction and experimental measurement. In this thesis, the homogeneous equation of state for liquid droplet model near the critical point does not provide complete information for the thermodynamics of the system. However, the proposed equation of state does contain the information for measurable quantities.

Thermodynamic Equilibrium[14,15]

A. Criteria of Stability

According to postulate 2, thermodynamic equilibrium is formally associated with the maximization of entropy. The basic extremum principle of thermodynamics implies that $dS = 0$ and that $d^2S < 0$. The condition that the entropy be a maximum is the requirement of stability of the predicted equilibrium states. Considerations of stability lead to some of the most interesting and significant predictions of thermodynamics.

In the last section we have discussed that the energy scheme and the Legendre transformation permit us to express the fundamental equation in terms of a set of independent variables chosen to be particularly convenient for a given problem. However, the advantage of being able to write the fundamental equation in various representations would be lost if the extremum principle were not itself expressible in those

representations. Therefore we would like to present the energy minimum principle in forms appropriate to the Legendre transformed representations.

The energy minimum principle states that the equilibrium value of any unconstrained internal parameter is such as to minimize the energy for the given value of the total entropy. The proof of the equivalence of the energy minimum principle and the entropy maximum principle can be found in references 13, 14 and 15. The minimum principle for different representations due to Legendre transformation will be listed in Appendix B.

B. Thermodynamic Conditions on Thermodynamic Equilibrium

The Equilibrium Conditions Due to the First Derivatives. In obtaining the conditions for thermal equilibrium from the condition of maximum entropy, we would require the first derivatives of entropy with respect to energy, volume and mole numbers to be zero. Therefore, for equilibrium, the temperatures, pressures, and chemical potentials will be the same at all parts of the composite systems under different conditions (constraints).

Let us consider an isolated composite system divided by diathermic rigid partitions into subsystems of constant volume and composition. Thus the extremum problem reduces to

$$S(U) = \max \sum_j S^{(j)}(U^{(j)}) \qquad (j) = \text{subsystem} \qquad (2\text{-}6)$$

under the constraint

$$\sum_j U^{(j)} = U = \text{Constant} \qquad (2\text{-}7)$$

For the sake of simplicity, we have suppressed the fixed variables $V^{(j)}$ and $N_k^{(j)}$. Let $\delta U^{(j)}$ be a virtual displacement leading from the equilibrium values U^j to the constrained equilibrium $U^{(j)} + \delta U^{(j)}$ with

$$\sum_{(j)} \delta U^{(j)} = 0 \tag{2-8}$$

The condition of equilibrium is

$$\delta S - \lambda \sum \delta U^{(j)} = \sum_{(j)} \left(\frac{\partial S^{(j)}}{\partial U^{(j)}} - \lambda \right) \delta U^{(j)} = 0 \tag{2-9}$$

where λ is the Lagrange multiplier associated with the constraint (2-8). Hence the condition (2-9) reduces to

$$\frac{\partial S^{(j)}}{\partial U^{(j)}} = \lambda \qquad j = 1, 2, \ldots \tag{2-10}$$

The parameter λ is common to all systems that are in thermal equilibrium with each other. From the definition of the temperature, we notice that the temperatures are the same at all parts of the composite systems that are in thermal equilibrium.

By the same token, for the constraint $\sum_j U^{(j)} = U$ and $\sum_j V^{(j)} = V$, we find the temperatures and the pressures at all parts of the composite systems that are in equilibrium having the same value. Or, for the constraint $\sum_j U^{(j)} = U$ and $\sum_j N_1^{(j)} = N_1$ (composite systems connected by rigid and diathermic wall, permeable to one type of material, N_1, and impermeable to all others, N_2, N_3, ..., N_k...), we find the temperatures and chemical potential for the first component μ_1^j at all parts of the composite systems that are in equilibrium having the same value.

The Equilibrium Condition due to the Second Derivatives.[16] The vanishing of the first derivatives of entropy with respect to energy, volume, and mole numbers is only a necessary condition for an extremum and does not ensure that the entropy is always a maximum. To obtain conditions for a maximum we are obliged to investigate the second derivatives of the function.

It is more convenient to carry out this investigation not by starting directly from the condition of the entropy maximum principle but from Gibbs function minimum principle (see Appendix B). Consider a system in contact with a temperature and a pressure reservoir, therefore for equilibrium the quantity $(U - T^rS + P^rV)$ is a minimum, where U, S, V are the energy, entropy, and volume of the given system and T^r and P^r are the temperature and pressure of the reservoir. From this consideration, the following conditions can be obtained:[16]

$$C_V > 0 \quad , \qquad \text{where } C_V \text{ is the specific heat at constant volume,} \tag{2-11}$$

and $$\left(\partial P/\partial V\right)_T < 0 \, . \tag{2-12}$$

Conditions (2-11) and (2-12) are called thermodynamic inequalities or convexity conditions for thermodynamic equilibrium.

Basis in Statistical Mechanics

Statistical physics is the study of the particular laws which govern the behavior and properties of macroscopic bodies. It has been a necessary tool for studying thermodynamics. Here we will briefly summarize the formulae of statistical thermodynamics in the following fashion that can be quoted throughout this thesis.

If a system had discrete quantum states 1, 2, 3, ... with energy E_1, E_2, E_3, ..., then the partition function Z_N is defined as the sum over all states i of the Boltzmann factor exp (- E_i/kT):

$$Z_N = \sum_{i=1}^{\infty} \exp\left(-E_i/kT\right) \tag{2-13}$$

In Equation (2-13) T is the temperature and K is Boltzmann's constant. The Helmholtz free energy F is related to the partition function by the equation

$$F = -KT \ln Z_N \tag{2-14}$$

Clearly, Z_N and F are functions of the temperature and of whatever other variables are needed to specify the system (volume V, number of molecules N for an assembly of N molecules in volume V). If the temperature is sufficiently high so that classical statistical mechanics can be used, the sum in Equation (2-13) can be replaced by an integral over all coordinates and momenta of the system. For a system of N molecules each of mass m in a volume V, the integration over the momenta can be performed immediately, leading to the following result:

$$Z_N = Q/\Lambda^{3N} \qquad \text{where} \quad \Lambda = \left(h^2/2\pi mKT\right)^{1/2} \tag{2-15}$$

Q is classical configuration integral, defined by the following equation:

$$Q_N(V,T,N) = \frac{1}{N!} \int \cdots \int_V \exp\left(-\Phi/kT\right) dq_1 \cdots dq_{3N} \tag{2-16}$$

where Φ is the total potential energy. Once free energy F is known as a function of N, V, and T, all the thermodynamic properties of the

system can be derived. Alternatively, one may form the grand canonical partition function

$$\Xi(T,Q,V) = \sum_{N=0}^{\infty} Z^N Q_N(T,Q,N) \tag{2-17}$$

where, in d dimensions, the activity z is related to the chemical potential μ by

$$z = \exp(\mu/kT)/\Lambda^d \tag{2-18}$$

and then derive thermodynamic properties from

$$P/kT = \frac{1}{V} \ln\{\Xi(T,z,Q)\} \tag{2-19}$$

The First-Order Phase Transition in Single-Component Systems

A. Phase Transition

The criteria of stability must be satisfied by the fundamental equation of any system that is to remain homogeneous and stable. If the stability criteria are not satisfied, the system breaks up into two or more portions in which they satisfy the stability criteria individually. The separation is called a PHASE TRANSITION. For a fluid, the intensive variables such as pressure P, temperature T and chemical potential μ remain the same during the transition, but the extensive parameters such as entropy S and volume V change their values during the transition. In other words, the first derivatives of a free energy of a system with respect to the intensive parameters are discontinuous functions; therefore it is called the first order phase transition.

Here we would like to outline some basic concepts concerning phase transition in the general formalism of statistical mechanics.

Thermodynamic Limit[17]. The statement of the 'limit' can be simply stated as the volume of the system and number of the system becomes infinite, with N/V fixed. However, whether or not the thermodynamic quantities after taking the thermodynamic limit still satisfy the thermodynamic theories has not yet been completely rigorously proved. Nevertheless, it is clear that without taking the thermodynamic limit we certainly cannot have a phase transition providing the molecular interaction has a sufficiently repulsive core.[6] This is simply because the integrand in Equation (2-16) is a bounded analytic function of T ($T > 0$, see postulate 2) and the domain of integration is finite, or in the quantum mechanical system the trace is merely the absolutely convergent sum of simple exponentials in T which is a non-negative quantity. (There is no real positive roots of the equation $\Xi = 0$ for any finite V.)

Yang and Lee's Theory[6,7]. In 1952, Yang and Lee examined the distribution of zeros of the grand partition function in the complex fugacity plane and the phase transition of a system of molecules with a hard core and finite-range attractive interaction. A complete description of the equation of state of both the gas and condensed phase can be obtained from the same interaction through the considerations of statistical mechanics, and it implies that mathematically the equation of state is represented by several analytical functions. The following two theorems form the basis of their idea.

Theorem 1. $\lim_{V \to \infty} \left[V^{-1} \ln \Xi(z, V) \right]$ exists for all $z > 0$. This limit is independent of the shape of the volume V and is a continuous, non-decreasing function of z. It is assumed that as $V \to \infty$ the surface

area of V increases no faster than $V^{2/3}$.

Theorem 2. Let R be a region in the complex z plane that contains a segment of the positive real axis and contains no root of the equation $\Xi(z,V)=0$ for any V. Then for all z in R the quantity $V^{-1}\ln\Xi(z,V)$ converges uniformly to a limit as $V\to\infty$. This limit is an analytic function of z for all z in R.

Van Hove's Theory[18]. The theory states that the equation of state in the canonical ensemble is the same as that in the grand canonical ensemble.

Van Hove's theory has direct physical meaning. The pressure of a macroscopic system should be the same, whether we measure it by confining the system with walls and measuring the force per unit area acting on the walls, or by probing a small volume in the interior of the system with a manometer. Thus Van Hove's theorem must be true, if statistical mechanics is to be a valid theory of matter.

B. Critical Point

There are many ways to define or determine a critical point. We can define it by varying the temperature or other thermodynamic parameters. Two distinct phases can frequently be made more and more similar in their properties until, ultimately, at a certain CRITICAL POINT, all differences vanish. Beyond this point only one homogeneous equilibrium phase can exist and all changes are continuous and smooth.

From analytical argument, we can find the critical point by 'hunting' the nearest singularity on the real positive axis. More precisely we should say that if the equation of state can be defined in the complex plane and in terms of a power series, then its analytic

continuation has, on the positive real axis, a nearest singularity which occurs at the condensation point. Of course, it is still a conjectured form, but nevertheless it is a very suggestive way to locate the critical point exactly.

From the stability criteria point of view, we can determine the critical point by checking the condition for critical stable equilibrium. It is found that the following conditions can be derived from the condition for the critical stable equilibrium[13,16]:

$$\partial P/\partial V)_{T_c} = \partial^2 P/\partial V^2)_{T_c} = 0 \qquad \partial^3 P/\partial V^3 < 0 \tag{2-20}$$

Here we would like to raise a controversial problem concerning whether the singularity appearing in the thermodynamic potential which locates the critical point is an essential singularity or not. Experimentalists have not been able to identify that the singularity is an essential singularity, but several theoretical proofs have shown that it is an essential singularity by different models.[19] However, there is no rigorous proof through statistical mechanics, therefore no conclusion can be made at this moment.

C. Properties of a Fluid near the Critical Point[3,8]

By experiments we observe that various thermodynamical quantities such as specific heats, density deviations from the critical point, etc. diverge to infinity or converge to zero as the temperature and other thermodynamic variable approaches its critical point value. It is appropriate to present a few mathematical definitions which enable critical behavior to be characterized numerically. A positive function f (x) is defined for a physical quantity near the critical point. If

it varies as x^{λ} when x approaches zero from above, we may write it more precisely as the following form:

$$\lim_{x \to 0^+} \left[\ln f(x) / \ln x \right] = \lambda \tag{2-21}$$

Of course the existence of the exponent does not mean that f(x) is simply proportional to x^{λ}. One must always expect correction terms of higher order. By this mathematical form we can define the critical exponents which characterize the properties of a fluid near the critical point.

Coexistence Curve. Approaching the critical temperature from below the fluid is characterized at T_c by the vanishing of the difference between the densities of gas and liquid coexisting at a chemical potential $\mu_\sigma(T)$ and pressure $P_\sigma(T)$. We define the exponent β and amplitude B by

$$\frac{\rho_c - \rho}{\rho_c} \simeq B \left(\frac{T_c - T}{T_c} \right)^{\beta} \tag{2-22}$$

Isothermal Compressibility K_T. Approaching the critical temperature from above, the critical point is most readily characterized by the divergence of the isothermal compressibility K_T

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T \tag{2-23}$$

On the critical isochore, $\rho = \rho_c$, this divergence may be described by

$$K_T \simeq \Gamma \left(\frac{T - T_c}{T_c} \right)^{-\gamma} \tag{2-24}$$

On the coexistence curve, this divergence may be described by

$$K_T \simeq \Gamma' \left(\frac{T_c - T}{T_c} \right)^{-\gamma'} \tag{2-25}$$

Critical Isotherm. Since K_T becomes infinite at the critical point, the critical isotherm (P vs V) becomes horizontal at the critical point. To describe its shape we may define an exponent δ as

$$p - p_c = \Delta (\rho - \rho_c) |\rho - \rho_c|^{\delta - 1} \qquad (T = T_c) \tag{2-26}$$

Specific Heat at the Constant Volume. Recently experiments have found that for various gases the specific heat at constant volume increases rapidly near T_c, apparently diverging to infinity in a roughly logarithmic manner.[4,8] We may write

$$\begin{aligned} C_V(\rho_c, T) &= -A^+ \log \left| 1 - \frac{T}{T_c} \right| + B^+ \quad , \; T > T_c \\ &= -A^- \log \left| 1 - \frac{T}{T_c} \right| + B^- \quad , \; T < T_c \end{aligned} \tag{2-27}$$

However, for the divergence more rapid than the logarithmic manner we define an exponent α as follows:

$$\begin{aligned} C_V(\rho_c, T) &= A^+/\alpha \left[\left(\frac{T_c - T}{T_c} \right)^{-\alpha'} - 1 \right] \quad T_c > T \\ &= A^-/\alpha \left[\left(\frac{T - T_c}{T_c} \right)^{-\alpha} - 1 \right] \quad T > T_c \end{aligned} \tag{2-28}$$

D. Inequalities for Critical Exponents

Recently it was discovered that certain quite general inequalities can be proved by thermodynamics (the convexity conditions for equilibrium), between the exponents α, β, γ, and δ. These results are rigorous and of wide application.

Rushbrooke inequality[20]: $$\alpha' + 2\beta + \gamma' \geq 2 \tag{2-29}$$

Griffiths inequality[21]: $$\alpha' + \beta(1+\delta) \geq 2 \tag{2-30}$$

Also, on the basis of heuristic arguments Widom[22] conjectured that the exponent for the critical isotherm, coexistence curve and isothermal compressibility were in general related by

$$\gamma' = \beta(\delta - 1) \tag{2-31}$$

Fisher[23] conjectured that the indices for the specific heat, coexistence curve and compressibility were in general related by

$$\alpha' + 2\beta + \gamma' = 2 \tag{2-32}$$

which is based on a phenomenological argument related to the Frenkel-Band[35,36] picture of condensation.

CHAPTER III

MOLECULAR FORCE AND PHASE TRANSITION

The first theory of phase transition was that of van der Waals. An essential equivalent (mathematically) thoery of spontaneous magnetization is associated with the names of Curie and Weiss and we also owe an almost identical theory of transition phenomena in binary alloys to Bragg and Williams. The van der Waals-like thoeries are based on the assumption that the attractive interactions are weak and of long range. These theories can be derived on the basis of a highly oversimplified molecular model, but basically it is a result of empirical curve fitting. For many simple substances the van der Waals-like theories represent the properties quite well above and below the critical point. However, their analysis has come under attack from both more precise experiments and more rigorous theories. The heat capacity measurements suggests that 'anomalies' near the critical point exist which are not present in their treatment and several theoretical models with finite range attractive forces presently available suggest 'anomalies' similar to those found in nature. Perhaps the strongest blow against these theories has come from Onsager's exact solution of the two-dimensional Ising model,[24] mainly because the rigorously established fact that the specific heat has a logarithmic singularity was in direct contradiction with predictions of the theories based upon the assumption of weak, long range forces, namely, that the specific heat has a jump discontinuity.

In this chapter we would like to discuss briefly these two models, especially their nature near the critical point. At the same time we shall get some insight about the well-known two problems in the study of the phase transition: WHAT ARE THE INTERACTIONS RESPONSIBLE FOR THE TRANSITIONS? HOW TO HANDLE THE STATISTICAL MECHANICS ONCE THE FORCES ARE KNOWN?

van der Waals' Theory

A. van der Waals' Equation of State

Van der Waals attempted to find a simple qualitative way to improve the equation of state of a dilute gas by incorporating the effects of molecular interaction. The result is the van der Waals' equation of state.

In most substances the potential energy between two molecules as a function of the intermolecular separation has the qualitative shape shown in the Figure 3-1. The attractive part of the potential energy originates from the mutual electric polarization of the two molecules and the repulsive part from the Coulomb repulsion of the overlapping electronic clouds of the molecules. Van der Waals idealized the situation by approximating the repulsive part by an infinite hard-sphere repulsion, so that the potential energy looks like that illustrated in Figure 3-2. Thus each molecule is imagined to be a hard sphere of diameter d, surrounded by an attractive force field. The effects of the repulsive and attractive parts are then discussed separately.

The main effect of the hard core would be to forbid the presence of any other molecule in a certain volume centered about a molecule. If

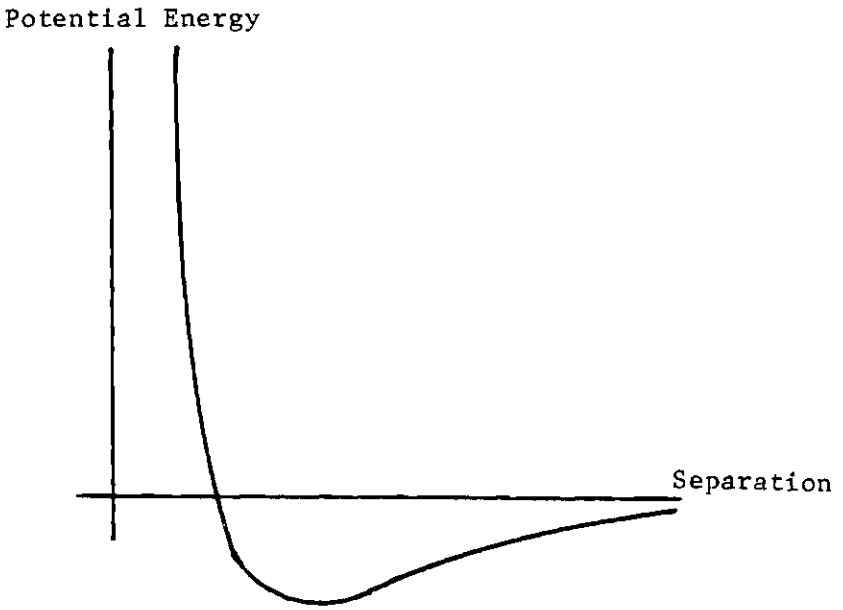


Figure 3-1. Typical Intermolecular Potential between Two Molecules

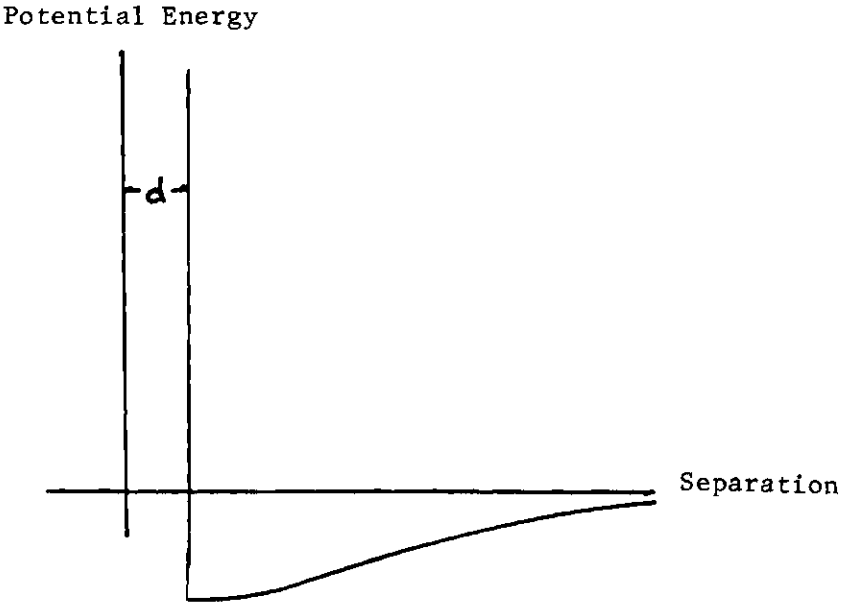


Figure 3-2. Idealized Intermolecular Potential

V is the total volume occupied by a substance, the effective volume available to one of its molecules would be smaller than V by the totality of such excluded volumes, which is a constant depending on the number of molecules present:

$$V_{eff} = V - b \tag{3-1}$$

where b is a constant characteristic of the substance under consideration.

The qualitative effect of the attractive part of the potential energy is a tendency for the system to form a bound state. If the attraction is sufficiently strong, the system will exist in an N-body bound state which requires no external wall to contain it. Thus we may assume that the attraction produces a decrease in the pressure that the system exerts on an external wall. The amount of decrease is proportional to the number of pairs of molecules, within the interaction range, in a layer near the wall. This in turn is roughly proportional to N^2/V^2. Since N and the range of interaction are constants, the true pressure P of the system may decomposed into two parts:

$$P = P_{kinetic} - a/V^2 \tag{3-2}$$

where a is another constant characteristic of the system and $P_{kinetic}$ is defined by the equation itself.

The hypothesis of van der Waals' is that for 1 mole of the substance

$$V_{eff}P_{kinetic} = RT \tag{3-3}$$

where R is the gas constant. Therefore the equation of state is

$$(V - b)(P + a/V^2) = RT \tag{3-3}$$

This is the VAN DER WALLS' EQUATION OF STATE.

B. Maxwell Construction and Stability Criterion for van der Waals' Equation of State

From the equation of state derived by van der Waals, we note immediately that the equation of state does not everywhere satisfy the criteria of intrinsic stability. For one of the criteria is that (see Equation 2-12)

$$(\partial P/\partial V)_T < 0$$

and this condition is violated over the portion FKM of a typical isotherm which is shown in Figure 3-3. A phase transition consequently must occur in this substance, and we shall see that the characteristics of this transition can be studied on the basis of the equation of state of Figure 3-3. The 'kink' in this typical isotherm may be attributed to the implicit assumption that the system is homogeneous, with no allowance made for the possible coexistence of two phases. The situation may be improved by making what is called a Maxwell construction in the following manner. We ask whether it is possible to have two different states of van der Waals' system coexisting in equilibrium. It is immediately obvious that for this to be possible the two states must have the same P and T. Therefore only states like those at volumes V_D, V_K, V_O in Figure 3-3 need be considered as candidates. The further

principle we apply is the minimization free energy. Let the temperature and the total volume of system be fixed. Then we assume the system is either in one homogeneous phase, or is composed of more than one phase. The situation that satisfies the minimum energy principle is the equilibrium state.

The free energy may be calculated by integrating PdV along an isotherm:

$$F(T,V) = -\int_{\text{isotherm}} PdV. \tag{3-5}$$

This may be done graphically, as shown in Figure 3-3b. It is seen that the state 0 and D can coexist because they have the same T and P (same slope). Further the point J' represents a state in which part of the system is in state 0 and part in state D, because the free energy of this state is a linear combination of those of 0 and D. We note that point j" lies lower than point J, which represents the free energy of a homogeneous system at the same T and V. Hence J', the phase separation case, is the equilibrium situation. Thus between the points 0 and D on the isotherm the system breaks up into two phases, with the pressure remaining constant. In other words, the system undergoes a first order phase transition. In the P-V diagram (Figures 3-3a) the point 0 and D are so located that areas A_1 and A_2 are equal. To show this, let us write down all the conditions determining 0 and D:

$$-\partial F/\partial V_0 = -\partial F/\partial V_D \qquad \text{(equal pressure)}$$

$$\frac{F_D - F_0}{V_D - V_0} = \partial F/\partial V_0 \qquad \text{(common tangent)}$$

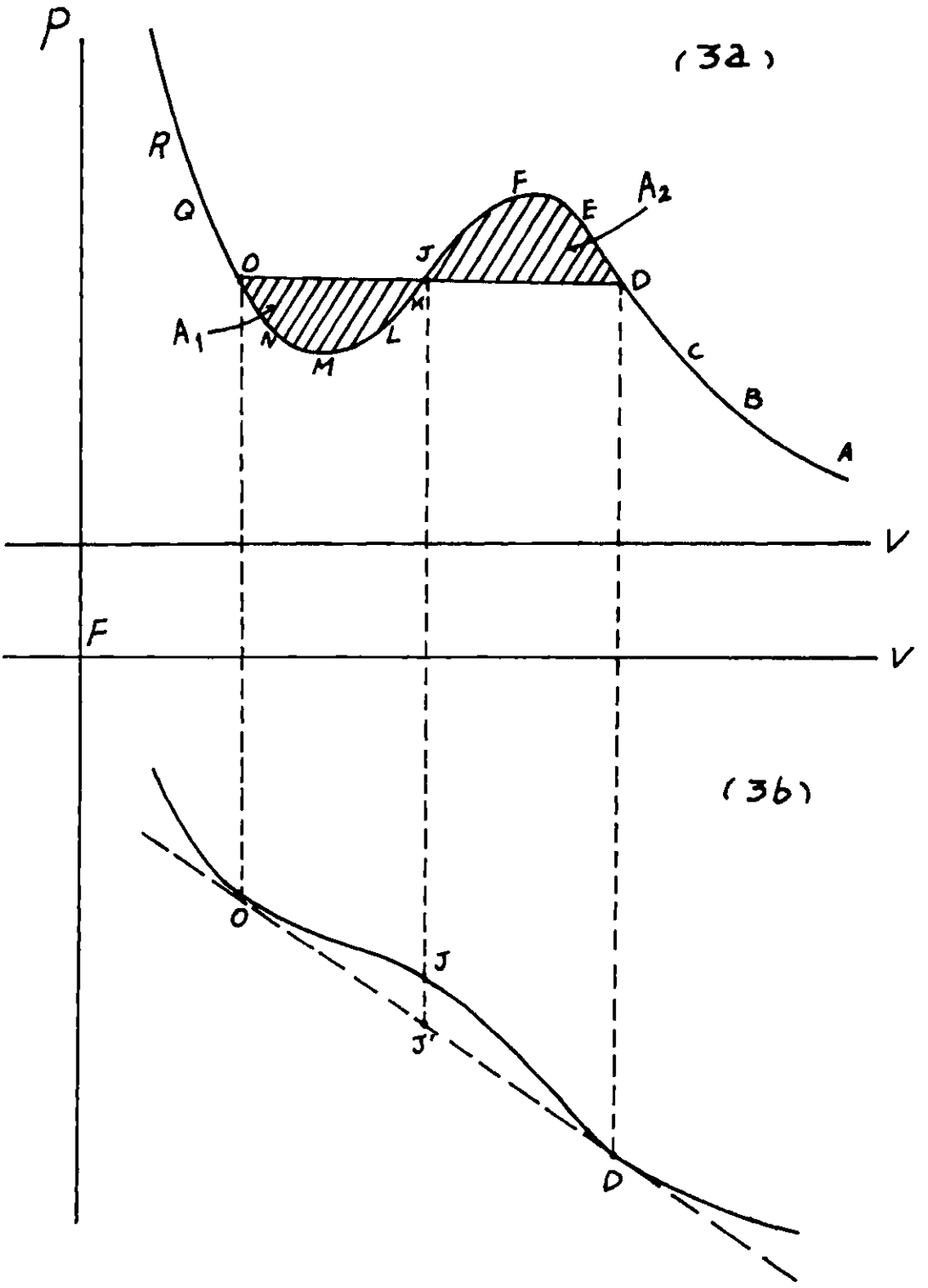


Figure 3-3. Maxwell Construction

Combining these we can write

$$(-\partial F/\partial V_0)(V_D - V_0) = -(F_D - F_0)$$

or

$$P_0(V_D - V_0) = \int_{V_0}^{V_D} P\, dV$$

whose geometrical meaning is precisely $A_1 = A_2$. The geometrical construction shown in Figure 3-3a is known as Maxwell construction.

The van der Waals' equation of state and the Maxwell construction are instructive examples, but they have no foundation other than a heuristic one. The hypothesis that led to the van der Waals' equation is ad hoc. The same may be said of the assumption underlying the Maxwell construction.

C. Critical Phenomena for the van der Waals' Equation of State

The Discontinuity in the Volume--the Lever Rule.[15] Consider the isotherm of Figure 3-3 and assume that a system has a pressure precisely equal to that at which the phase transition occurs. Then the system may equally well be in the state D or in the state 0, or any arbitrary fraction of the system may be in the state D and the remainder in the state 0. If fraction f_D of a system is the less condensed phase, in equilibrium with a fraction f_0 in the more condensed phase, where $f_D + f_0 = 1$, the average molar volume v_T of the total system is clearly

$$v_T = f_D v_D + f_0 v_0 \tag{3-6}$$

$$= v_0 + f_D(v_D - v_0) \tag{3-7}$$

The state of such a mixture is represented by a point at the appropriate value of v on the straight line connecting the points 0 and D, as shown by the state T in Figure 3-3. The relationship of such a state, representing a two phase system, and the mole fractions of each of the phases, is expressed by the lever rule which states that the mole fractions of the two phases represented by the point T are in inverse ratio to the distances from T to the points 0 and D.

We have

$$f_0/f_D = (v_D - v_T)/(v_T - v_0) \tag{3-8}$$

From this we can conclude that although the volume of a system is mathematically discontinuous function of the pressure along the isotherm, this is not necessarily a physically discontinuous process. A system brought along the isotherm from A to S changes its total volume continuously, holding its pressure constant while passing from D to 0 and taking advantage of the coexistence of two phases, which is possible at that particular pressure.

The Discontinuity of the Entropy--Latent Heat. We mentioned in Chapter II for the first order phase transition that not only is there a nonzero change in the volume, but there are associated nonzero changes in the molar energy and the molar entropy as well. The change in the entropy can be computed by integrating the quantity

$$ds = \frac{\partial S}{\partial V}\Big)_T dv \tag{3-9}$$

along the isotherm OMKFD in Figure 3-3a. By Maxwell's relation, $(\partial S/\partial V)_T = (\partial P/\partial T)_V$, alternatively, we can write

$$\Delta S = S_D - S_o = \int_{OMKFD} \left(\frac{\partial P}{\partial T}\right) dV \qquad (3\text{-}10)$$

A geometrical interpretation of this entropy difference, in terms of the area between neighboring isotherms, is shown in the Figure 3-4. The change in the molar entropy is associated with a flux of heat between the system and the reservoir. The heat is simply $T\,\Delta S$ and is called the latent heat per mole ℓ. To be explicit, we shall indicate the order in which the molar entropies appear on the right by subscripts on ℓ :

$$\ell_{DO} = T(S_D - S_O) \qquad (3\text{-}11)$$

Thus ℓ_{DO} is the heat emitted by a mole of material making the transition from D to 0. As the system is transformed at fixed temperature and pressure from the pure phase 0 to the pure phase D, it absorbs an amount of heat per mole equal to $\ell_{DO} = T\,\Delta S$. The volume change per mole is $\Delta V = V_D - V_0$, and this is associated with a transfer of work equal to $P\,\Delta V$. Consequently, the total change in the molar energy is

$$\Delta U = U_P - U_0 = T\Delta S - P\Delta V \qquad (3\text{-}12)$$

Phase Loci--Coexistence Curve. As indicated in Figure 3-3, we have seen that the stability criteria enable us to classify the isotherm shown into three portions. The portion to the left of 0 is associated with one phase, liquid phase; the portion OMKFD is rejected as unstable, by Maxwell construction we get the coexisting two phase equilibrium

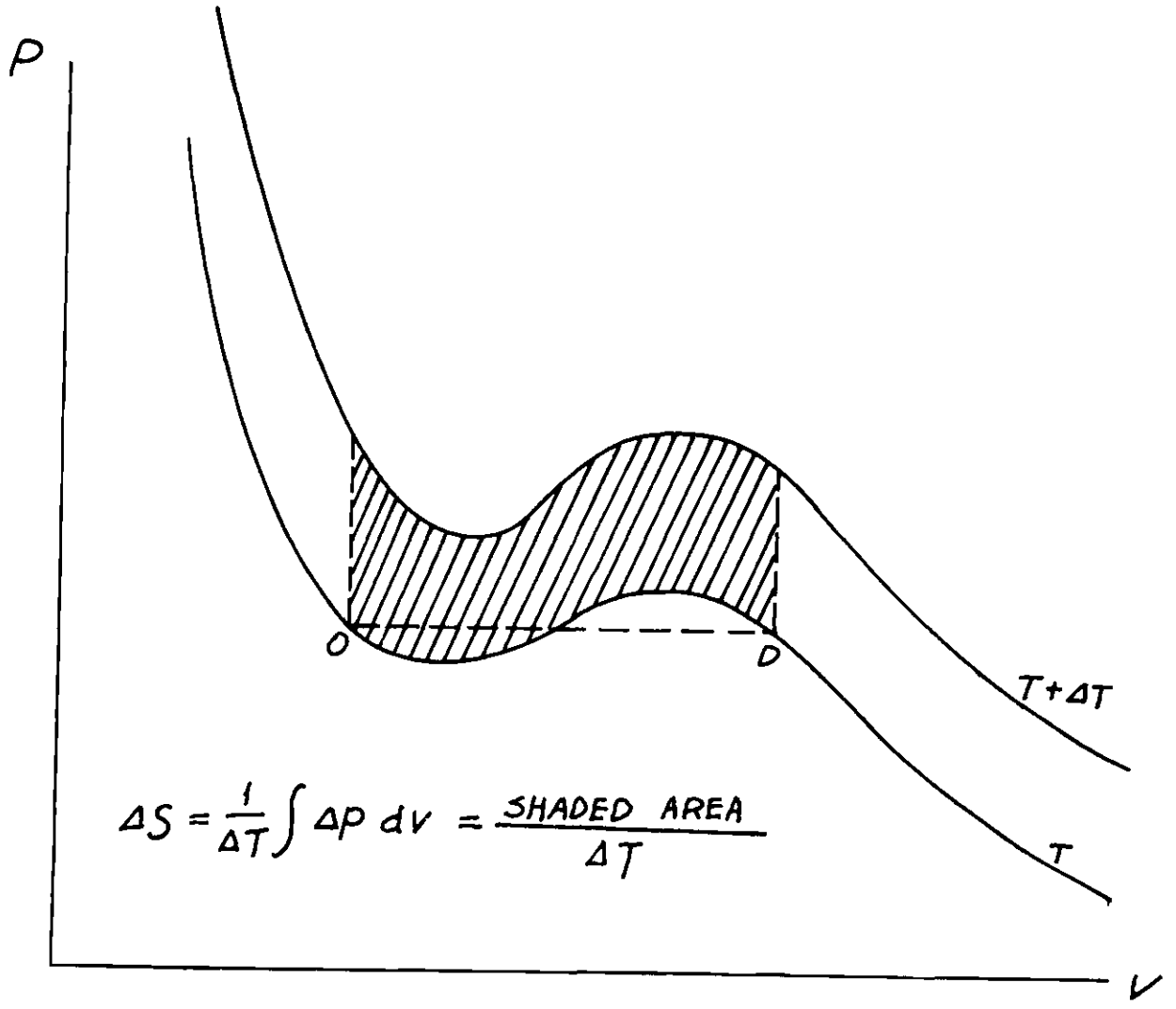


Figure 3-4. Geometrical Interpretation of the Entropy Difference between Different Isotherms

state, whereas the portion to the right of D is associated with a second phase, gaseous phase. The total P-V diagram may be divided accordingly by drawing a curve through the phase transition points O and D of each isotherm, as indicated in Figure 3-5. Then a system with pressure P and molar volume V in the lower far right portion is in the gaseous phase; in the lower left portion it is in the liquid phase, and within the inverted parabola-like locus it is a mixture of liquid and gaseous phases in accordance with the lever rule. The inverted parabola-like curve is known as the coexistence curve, and the point O_3D_3 in Figure 3-5 is known as the critical point. As pointed out in the last section, the system led from the liquid to the gaseous regions by a path that transforms continuously and smoothly without undergoing any discontinuous alteration in its physical process for temperatures above T_0.

Critical Point of the van der Waals' Equation of State. In Chapter II we noticed that the critical point for a simple system can be determined by Equation (2-20). Apply the condition (2-20) to the van der Waals' equation of state, Equation (3-4), we can therefore find the critical temperature, critical volume and critical pressure in terms of van der Waals' constant a and b, we have

$$RT_c = 8a/27b \ , \ P_c = a/27b^2, \ V_c = 3b \qquad (3\text{-}13)$$

Let us measure P in units of P_c, T on units of T_c, and V in units of V_c:

$$\bar{P} = P/P_c \ , \ \bar{T} = T/T_c \ , \ \bar{V} = V/V_c \qquad (3\text{-}14)$$

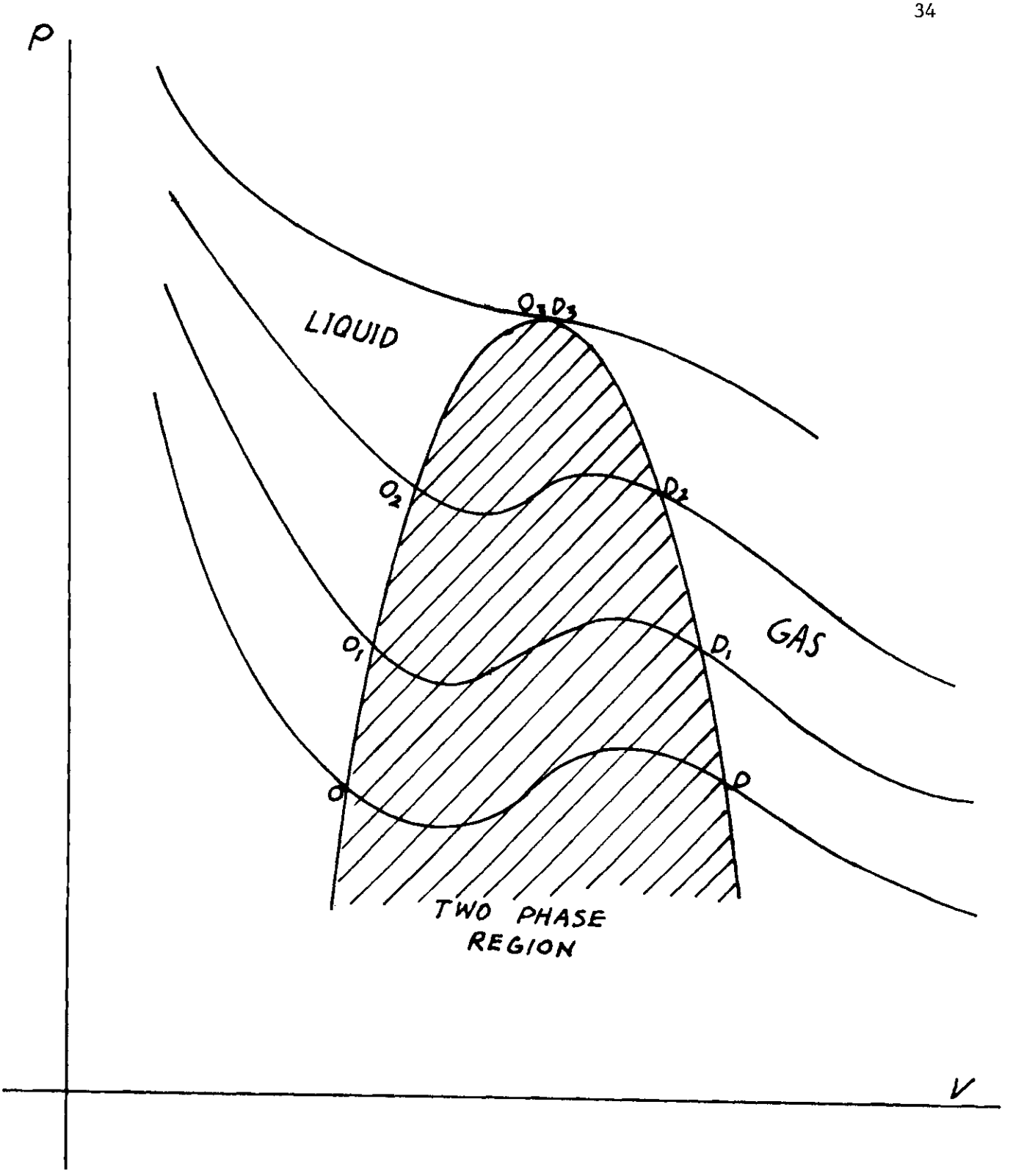


Figure 3-5. P-V Diagram of the van der Waals Equation of State

Then the van der Waals' equation of state becomes

$$(\bar{P} + 3/V^2)(\bar{V} - 1/3) = 8/3\bar{T} \qquad (3\text{-}15)$$

This is a REMARKABLE equation because it does not explicitly contain any constant characteristics of the substance. If the van der Waals' hypothesis were correct, Equation (3-15) would hold for all substances. The assertion that the equation of state when expressed in terms of $\bar{P}$, $\bar{V}$, and $\bar{T}$ is a universal equation valid for all substances is called the law of corresponding states.

Properties near the Critical Point for the van der Waals' Theory. From Chapter II, we know the critical exponents α, β, γ, and δ describe the thermodynamic behavior in the vicinity of the critical point. Here we simply state the results of these critical exponents derived from Equations (3-4), (3-13) and the definitions of the thermodynamic qualities such as isothermal compressibility, specific heat at constant volume, etc.

The Coexistence Curve: the coexistence curve for the van der Waals' theory follows a squareroot law, i.e. the difference between liquid and gaseous densities vanishes as

$$P_L - P_G = (T_c - T)^{\frac{1}{2}} \quad (T \rightarrow T_c-); \qquad (3\text{-}16)$$

the critical exponent

$$\beta = 1/2 \qquad (3\text{-}17)$$

The Isothermal Compressibility K_T: the compressibility along the critical isochore diverges as a simple pole,

$$K_T = -\frac{1}{V}\frac{\partial V}{\partial P}\Big)_T \sim \frac{1}{|T-T_c|} \quad (\rho=\rho_c,\ T\to T_c^+); \tag{3-18}$$

the critical exponent

$$\gamma = 1 \tag{3-19}$$

The Specific Heat at Constant Volume C_v: the specific heat at constant volume along the critical isochore rises to a maximum and then falls discontinuously as T increases through T_c, i.e.

$$C_V(T) \sim C_c^{\pm} - D^{\pm}|T-T_c|, \quad T \gtrless T_c$$

with

$$C_c^- - C_c^+ = \Delta C > 0 \tag{3-20}$$

the critical exponent

$$\alpha = 0_{\text{discon.}} \tag{3-21}$$

The Critical Isotherm: the sahpe of the critical isotherm can be described by the following relation:

$$\Delta P = |P-P_c| \simeq \Delta|\rho-\rho_c|^3 \tag{3-22}$$

the critical exponent

$$\delta = 3 \tag{3-23}$$

Relations among the Critical Exponents: the critical exponents for the van der Waals' theory satisfy the following relationships:

$$\alpha + 2\beta + \gamma = 2 \tag{3-24}$$

$$\gamma = \beta(\delta - 1) \tag{3-25}$$

These two equalities satisfy both Widom and Fisher's conjectures, given in Equations (2-31) and (2-32).

D. Recent Development of the van der Waals' Theory

Kac, Hemmer and Uhlenbeck.[3,25] In 1963, Kac, Hemmer and Uhlenbeck have a series of discussions of the van der Waals' theory of the vapor-liquid equilibrium by use of a one-dimensional fluid model where the pair interaction potential between the molecules consist of a hard core and an exponential attraction. For this one dimensional model, they have shown that the partition function can be determined exactly in the thermodynamic limit, in the so-called van der Waals' limit when the range of the attractive force goes to infinity while its strength becomes proportionally weaker. A phase transition appears which is described exactly by the van der Waals' equation plus the Maxwell equal-area rule (Maxwell construction). The main tool of their analysis can be briefly discussed in the following fashion: the partition function of this particular model can be exactly determined in the thermodynamic limit as an integral equation. From this basic integral equation, an appropriate perturbation method is applied along with the van der Waals' limit. It is seen that the phase transition persists in any order of the pertur-

bation. The two phase equilibrium is characterized by the fact that in this range of density, the maximum eigenvalue of the integral equation is doubly degenerate and that the corresponding two distribution functions of particles do not overlap. Their analysis provides the first rigorous statistical mechanical basis for van der Waals' equation of state.

Lebowitz and Penrose.[26] In 1966 Lebowitz and Penrose extended Kac, Hemmer, and Uhlenbeck's work to higher dimensions and to more general interparticle potentials of the form $v(r) = q(r) + \gamma^{\nu}\varphi(\gamma r)$, where ν is the dimensionality of the space, and parameter γ is proportional to the reciprocal of the interaction range. In this work, it is proven rigorously for a wide class of q's and φ's that in the van der Waals' limit $\gamma \to 0$, the equation of state will have the form

$$\lim_{\gamma \to 0} P(\rho, \gamma) = P^{0}(\rho) + \frac{\alpha}{2}\rho^{2}$$

where $P^{0}(\rho)$ is the pressure in the reference system, for which $\varphi(r) = 0$, and $\alpha \equiv \int \varphi(y)dy$. In this paper, rigorous upper and lower bounds were obtained for the thermodynamic free energy density of a system with 'van der Waals-like molecular interaction.' The quantum system for this kind of molecular interaction has also been derived and proved by Burke, Lebowitz and Lieb.[27]

Ising Model

A. Introduction of Ising Model[17,28]

One of the most interesting phenomena in the physics of the solid state is ferromagnetism. In some metals, a finite fraction of

the spins of the atoms becomes spontaneously polarized in the same direction, giving rise to a macroscopic magnetic field. This happens only when the temperature is lower than a characteristic temperature known as the Curie temperature. Above the Curie temperature the spins are oriented at random, producing no net magnetic field, as the Curie temperature is approached from both sides the specific heat of the metal approaches infinity. The transition from the nonferromagnetic state to the ferromagnetic state is a phase transition of a type not included within the usual classifications. The Ising model is a crude attempt to simulate the structure of a physical ferromagnetic substance. Its main virtue lies in the fact that a two-dimensional Ising model yields to an EXACT treatment in statistical mechanics. It is the only non-trivial example of a phase transition that has been worked out with mathematical rigor.

In the Ising model the system considered is an array of M fixed points called lattice sites that form an n-dimensional periodic lattice (n = 1, 2, 3). The geometric structure of the lattice may be cubic, hexagonal, etc. Associated with each lattice site is a spin variable s_i (i = 1, 2, ..., N) which is a number that is either +1 or -1. There are no other variables. If $s_i = +1$, the ith site is said to have spin up, and if $s_i = -1$, it is said to have spin down. A given set of numbers (s_i) specifies a configuration of the whole system. The energy of the system in the configuration specified by (s_i) is defined to be

$$E_I(S_i) = -\sum_{\langle ij \rangle} \epsilon_{ij} S_i S_j - B \sum_{i=1} S_i \qquad (3\text{-}26)$$

where the subscript I stands for Ising and the symbol $\langle ij \rangle$ denotes a nearest neighbor pair of spins. There is no distinction between $\langle ij \rangle$ and $\langle ji \rangle$. Thus the sum over $\langle ij \rangle$ contains $b\,N/2$ terms, where b is the number of nearest neighbors of any given site. For example,

$$b = \begin{cases} 4 \text{ (two-dimensional square lattice)} \\ 6 \text{ (three-dimensional simple cubic lattice)} \\ 8 \text{ (three-dimensional body-centered cubic lattice)} \end{cases}$$

The interaction energy ϵ_{ij} and the external magnetic field B are given constants. The geometry of the lattice enters the problem through b and ϵ_{ij}. For simplicity we specialize the model to the case of isotropic interactions, so that all ϵ_{ij} are equal to a given number ϵ. Thus the energy will be taken as

$$E_I = -\epsilon \sum_{\langle ij \rangle} S_i S_j - B \sum_{i=1}^{N} S_i \tag{3-27}$$

The case $\epsilon > 0$ corresponds to ferromagnetism and the case $\epsilon < 0$ to antiferromagnetism. We consider only the case $\epsilon > 0$. The partition function is

$$Q_I(B,T) = \sum_{S_1} \sum_{S_2} \cdots \sum_{S_N} e^{-E_I/KT} \tag{3-28}$$

where each s_i ranges independently over the values +1. Hence there are 2^M terms in the summation. The thermodynamic functions are obtained in the usual manner from the Helmholtz free energy:

$$A_I(B,T) = -KT \log Q_I(B,T) \tag{3-29}$$

B. Equivalence of the Ising Model to Lattice Gas Model[7,17]

By a change of names the Ising model can be made to simulate other systems than a ferromagnet. Among these are a lattice gas and a binary alloy. In this section we emphasize relatively more detail about the lattice gas system.

A lattice gas is a collection of atoms whose positions can assume only discrete values. These discrete values form a lattice of given geometry with nearest neighbors to each lattice site. Each lattice site can be occupied by at most one atom. We neglect the kinetic energy of an atom and assume that only nearest neighbors interact, and the interaction energy for a pair of nearest neighbors is assumed to be a constant $-\epsilon_o$. Thus the potential energy of the system is equivalent to that of a gas in which the atoms are located only on lattice sites and interact through a two-body potential $u(|\vec{r}_i - \vec{r}_j|)$ with

$$u(r) = \begin{cases} \infty & (r = 0) \\ -\epsilon_o & (r = \text{nearest-neighbor distance}) \\ 0 & (\text{otherwise}) \end{cases} \qquad (3\text{-}30)$$

Let N = total number of lattice sites

N_a = total number of atoms (3-31)

N_{aa} = total number of nearest neighbor pairs of atoms

The total energy of the lattice gas is

$$E_G = -\epsilon_o N_{aa} \qquad (3\text{-}32)$$

and the partition function is

$$Q_G(N_a, T) = \frac{1}{N!} \sum^{a} \exp(-\epsilon_o N_a / kT) \qquad (3\text{-}33)$$

where $\sum^{a}$ extends over all ways of distributing N_a distinguishable atoms over N lattice sites. If the volume of a unit cell of the lattice is chosen to be unity, then N is the volume of the system. The grand partition function is

$$\Xi_G(z, N, T) = \sum_{N_a=0}^{\infty} z^{N_a} Q_G(N_a, T) \tag{3-34}$$

The equation of state is given by

$$\begin{aligned} P_G/kT &= \frac{1}{N} \log \Xi_G(z, N, T) \\ \frac{1}{V} &= \frac{1}{N} z \frac{\partial}{\partial z} \log \Xi_G(z, N, T) \end{aligned} \tag{3-35}$$

To establish a correspondence between the lattice gas and Ising model, let occupied sites correspond to spin up and empty sites to spin down. In the Ising model a set of N numbers (s_i, ..., s_N) uniquely defines a configuration. In the lattice gas an enumeration of the occupied sites determines not one but $N_a!$ configurations. The difference arises from the fact that atoms are supposed to be able to move from site to site. This difference, however, is obliterated by the adoption of correct Boltzmann counting. The correspondence between a lattice gas and an Ising magnet will be listed in the Table 1. As for the equivalence between Ising model and the binary alloy, we simply make the correspondence that the number of up spins is equivalent to the one kind of atoms and the down spins to the other kind of atoms.

C. Molecular Field Approximation (Weiss Theory, Bragg-Williams Approximation)

The idea of a molecular field (mean field) is most familiar in

Ising Model	Lattice Gas
Total number of up spins N_+	Total number of atoms N_a
Total number of down spins N_-	Total number of unoccupied sites $N-N_a$
Interaction energy 4ϵ	ϵ_a
Magnetic field $\exp\left[\frac{2(\epsilon b - B)}{kT}\right]$	Fugacity z
$-\left(A_I/N + \frac{1}{2}b\epsilon - B\right)$	Pressure P_G
$\frac{1}{2}\left(M_z/N + 1\right)$	Density
Spontaneous Magnetization M	Density deviation
Zero magnetic field M = 0	Critical isochore
Curve of spontaneous Magnetization	Coexistence curve

the study of magnetism, exact same role played by van der Waals' theory in the fluids, where it was first introduced by Pierre Weiss in 1907. Here we would like to derive this approximation in two ways in order to grasp some concepts about the 'mean field' and so-called van der Waals-like result.

Self-Consistent Field Method. Equation (3-27) may be looked upon as the statement that a spin, say s_i, 'feels' a field B_i, where

$$B_i = \left(\epsilon \sum_j S_j \right) + B \tag{3-36}$$

The average field is

$$\langle B_i \rangle = \langle \epsilon \sum \langle S_j \rangle \rangle + B \tag{3-37}$$

Since the Ising model provides the translational symmetry, the average value of s_j is independent of the index j. Call it $\bar{L}$ where $-1 \leq \bar{L} \leq +1$. $\bar{L}$ is called either long-range order or average magnetization. Then Equation (3-37) becomes

$$\langle B_i \rangle = b\epsilon\bar{L} + B \tag{3-38}$$

The Weiss approximation consists in assuming that the field at point i is $\langle B_i \rangle$ independent of the orientation of s_i. This is an approximation, for if s_i is up, its neighbors (s_i) will have more than average prediction for being up, a fluctuation effect that is neglected in the Weiss assumption. Given the approximation, it is a straightforward matter to calculate $\langle s_i \rangle$ according to

$$\bar{L} = \langle S_i \rangle = \operatorname{tr} S_i \exp[S_i \langle B_i \rangle / \kappa T] / \operatorname{tr} \exp[S_i \langle B_i \rangle / \kappa T]$$

$$= \tanh\left[\frac{b\epsilon \bar{L} + B}{\kappa T}\right] \tag{3-39}$$

We then have a self-consistent equation

$$\bar{L} = \tanh\left[(b\epsilon \bar{L} + B)/\kappa T\right] \tag{3-40}$$

Bragg-Williams Approximation. We would like to take this opportunity to discuss the long range order and short range order which we have mentioned in the last section. In the Ising model the energy of a configuration of the spin lattice depends not on the detailed distribution of spins over lattice sites but only on the two numbers N_+, total number of up spins, and N_{++}, total number of nearest-neighbor pairs of up spins, which express certain gross features of the spin distribution. The number N_+/N is said to be a measure of the long-range order in the lattice, and $N_{++}/(b\,N/2)$ is said to be a measure of the short-range order. We shall discuss briefly the reason in the following. Let us imagine that the distribution of the spin is random, except for the restriction that it possesses the given values of N_+ and N_{++}. If we know definitely that a given spin is up, then the number $N_{++}/(b\,N/2)$ is the fraction of its nearest neighbors with spin up. This number, however, imposes less and less correlation as we consider the second nearest neighbors, thirs nearest neighbors, etc. It is therefore a measure of the local correlation of the spins; hence the name short-range order. On the other hand, the number N_+/N requires no correlation between nearest neighbors. It does require in the entire lattice a fraction N_+/N of all the spins are up.

Thus if the number N_+/N is known in the neighborhood of a given spin, we will know that no matter how far we go away from the given spin the order measured by it is the same. Hence the name long-range order.

Here we define the parameter of long-range order L as

$$N_+/N = 1/2(L + 1) \quad (-1 \leq L \leq +1) \tag{3-41}$$

The Bragg-Williams approximation is contained in the statement that "there is no short-range order apart from that which follows from long-range order." More precisely, the approximation consists of putting $N_{++}/(\epsilon N/2) \simeq (N_+/N)^2$. In this approximation the energy, Equation (3-27), becomes

$$1/N\ E_I(L) \simeq -1/2\ \epsilon\ L^2 - BL \tag{3-42}$$

The entropy can be calculated by counting the number of configurations that we pick N_+ things out of N, namely $N!/[N_+!(N - N_+)!]$ The free energy is then

$$A_{I(BW)} = - (N\epsilon/2)L^2 - NLB - kT \log \frac{N!}{\{[N(1+L)/2]![N(1-L)/2]!\}} \tag{3-43}$$

After use of Stirling's approximation for treating N!, we minimize the free energy with respect to L and the Equation (3-40) is recovered, where $\bar{L}$ is the value of L which minimized the free energy.

C. Critical Phenomena of Molecular Field Approximation

We consider the case of no external field (B = 0). Then Equation (3-27) becomes

$$\bar{L} = \tanh(b\epsilon\bar{L}/kT) \tag{3-44}$$

which may be solved graphically as indicated in Figure 3-6.

If $\epsilon > 0$, there exists a critical temperature T_c, given by

$$kT_c = b\epsilon \tag{3-45}$$

such that

$$\bar{L} = \begin{cases} 0 & (T > T_c) \\ \pm L_o & (T < T_c) \end{cases} \tag{3-46}$$

where L_o is the root of Equation (3-44) that is greater than zero. The temperature T_c is the Curie temperature of the system, since for $T < T_c$ the system is a ferromagnet. The degeneracy arises from the fact that in the absence of an external magnetic field there is no intrinsic distinction between up and down.

From Equation (3-43) we can derive the equation of state of the system, we have

$$P = B - \frac{\epsilon b}{8}(1+\bar{L}^2) - kT/2 \log\left[(1-\bar{L}^2)/4\right] \tag{3-47}$$

After translating into lattice gas language, we have

$$P = -\frac{\epsilon_o}{2}\rho^2 - kT \log(1-\rho) \tag{3-48}$$

If we compare this equation with the van der Waals' equation of state, we will find that the only difference is the way they handle the pressure of the hard-core. So, we shall easily expect the properties of the critical

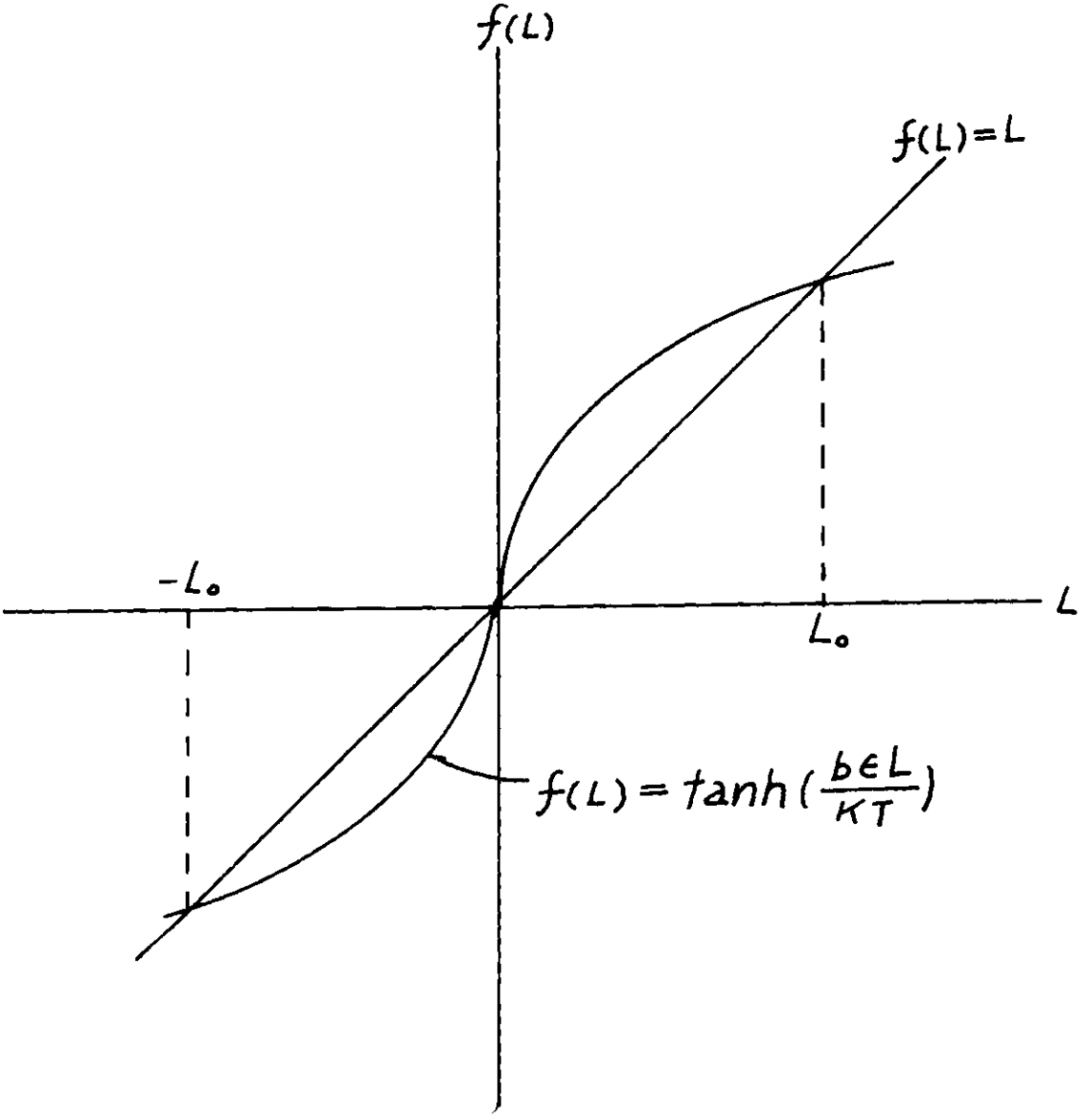


Figure 3-6. Graphical Solution of Equation (3-44)

phenomena of the molecular field approximation is very similar to the van der Waals' theory which we have derived before. Certainly, the critical exponents derived by both theory have the same values, and Maxwell Construction is also required in the molecular field approximation to establish the stability criteria.

D. The Onsager Solution[24]

The first crucial step for Ising model was Onsager's (1944) exact calculation of the partition function of the plane square lattice in zero field with two-dimensional interaction parameters: ϵ_x for horizontal and ϵ_y for vertical bonds. In this calculation Onsager has exhibited clearly how a phase transition would come out of statistical mechanics alone if only one were clever enough to compute the partition function precisely: there is no need of any additional assumptions, as we did for Weiss theory, special procedures or the like. However, we shall not here discuss the detailed mathematical techniques used to solve this problem; in the first place, these are still rather elaborate, but secondly, they in themselves cast little light on the behavior near the critical point. Therefore, we simply start from the explicit expression of the free energy

$$-A(T)/kT = \frac{1}{2}\int_{-\pi}^{\pi}\frac{d\theta_1}{2\pi}\int_{-\pi}^{\pi}\frac{d\theta_2}{2\pi}\ln\left(\cosh 2K_x \cosh 2K_y - \sinh 2K_x\cos\theta_1 - \sinh 2K_y\cos\theta_2\right) \quad (3\text{-}49)$$

for the limiting free energy per spin, where

$$K_x = \frac{\epsilon_x}{kT} \quad , \quad K_y = \frac{\epsilon_y}{kT} \quad (3\text{-}50)$$

it is easily seen that there is a singularity at a critical temperature

determined by

$$\sinh\left(\frac{2\epsilon_x}{KT_c}\right)\sinh\left(\frac{2\epsilon_y}{KT_c}\right) = 1 \tag{3-51}$$

At this point the argument of the logarithm in Equation (3-49) vanishes quadratically with T, whence it follows that, as $T \rightarrow T_c \pm$,

$$A(T) = A_c + a(T - T_c) + b(T - T_c)^2 \ln|T - T_c| + \cdots\cdots \tag{3-52}$$

where a and b are constant depending on ϵ_x and ϵ_y. The appearance of the logarithmic factor in the second-order term proves that the free energy (zero field) has no Taylor-series expansion about $T = T_c$.

Differentiation of Equation (3-51) shows that the internal energy varies as

$$U(T) = U_c + A K(T_c - T)\ln\left|1 - \frac{T}{T_c}\right| + \cdots\cdots \quad (T \rightarrow T_c) \tag{3-53}$$

and so has a vertical tangent at $T = T_c$. It also follows that the specific heat exhibits a symmetric logarithmically infinite singularity of the form

$$C_B(T)/K = A\left|\ln\left|1 - \frac{T}{T_c}\right|\right| - A_1 + O\left\{(T - T_c)\ln|T - T_c|\right\} \tag{3-54}$$

so that the critical exponent

$$\alpha = 0_{\log} \tag{3-55}$$

This is in marked contrast to the van der Waals' prediction of a finite, discontinuous and hence, asymmetric anomaly. However, this exact result also contrasts with the asymmetric, although near-logarithmic, experimental data.

E. Properties near the Critical Point for the

Two-Dimensional Ising Model

Historically the next significant thermodynamic result was the expression

$$M_o(T) = \left\{ 1 - (\sinh 2K_x \sinh 2K_y)^{-2} \right\}^{\frac{1}{8}} \qquad (3\text{-}56)$$

for the spontaneous magnetization of the plane square lattice.[29] From this we have the second critical exponent

$$\beta = 1/8 \qquad (3\text{-}57)$$

We notice that it is again sharply different from the classical result which is 1/2. With this result and Equation (3-55) we may apply the rigorous inequalities Equations (2-68) and (2-69) to reach the conclusion

$$\gamma \geq 7/4^{(8)} \qquad (3\text{-}58)$$

$$\delta \geq 15^{(8)} \qquad (3\text{-}59)$$

If we apply the conjectures made by Widom and Fisher[22,23] the equalities will hold, and numerical study suggested the equality should be the 'best possible.'

F. Recent Development of Lattice Gas Model

As we mentioned in the previous section, the analytic theory of Ising model is restricted almost entirely to two-dimensional systems, even though it reveals unequivocally the theoretical shortcoming of the classical approaches. No exact expressions for the partition function of any two dimensional lattices in a finite magnetic field have been

found; no exact solution for the partition function of any three-dimensional lattices has been established. Nevertheless, the group recognized as 'theoretical experimentalists' in England has offered their numerical analysis by series expansion which provides some very good qualitative and quantitative information about the phase transition for fluids and ferromagnetic materials.[8,30] Their main philosophy is that "given a bounded Hamiltonian a formal high-temperature expansion in powers of 1/T may always be constructed by expanding the Boltzmann factor and taking the trace term by term. It is to be anticipated that for sufficiently short-range interactions one will be able to prove rigorously that the resulting series expansion for the free energy converges absolutely for sufficiently high temperature." By this, extensive studies of combinatorial problems have been done by direct enumeration, by Monte Carlo techniques[8] and by rigorous analysis. Ratio test[8,30] and Pade' approximation[8,31] have been also widely used.

Quantum lattice gas model was introduced by Matsubara and Matsuda[32] in 1956. The equivalence between the quantum lattice gas model and the Heisenburg-Ising model has been established.[8] However, the exact solution in two and three dimensional lattices still is an open problem. Another Onsager is urgently needed to stand on the shoulder of the giant.

CHAPTER IV

CLUSTER THEORY AND CONDENSATION

In this chapter we give a discussion of the cluster theory and investigate how far this theory may be used for describing the critical phenomena. For the cluster theory, unlike the treatment of the last chapter, very little progress has been made in the way of calculating thermodynamic functions numerically and therefore the analysis is rather formal. It is also generally agreed that this theory is not applicable in its present form to the liquid state. In spite of these deficiencies, the cluster theory offers considerable insight into the nature of condensation. In the meantime, due to the failure of the 'classical approaches' (van der Waals' theory and molecular field approximations), the reconsideration of the cluster theory may cast some light on the explanation of the phenomena near the critical region.

Many contributions have been made for the cluster theory, and a detailed discussion on this matter can be found in the paper entitled "On the Theory of the Equation of State" by Boris Kahn.[33] In this chapter, therefore, we shall not go through all the rigorous formalisms but merely consider the possible application of the cluster theory for the phenomena near the critical region. With this in mind, we will briefly present Mayer's theory,[34] the approximate cluster theory introduced by Frenkel,[35] and Band,[36] and the modified liquid droplet model proposed by Fisher.[10] At the same time, some discussions of the phenomena near the critical region for these theories or models will be carried on in this

chapter.

Mayer's Theory of Imperfect Gases and Condensation[34]

A. Cluster Integrals

With the assumption of pairwise interactions for a system composed of N idential molecules, Equations (2-15), (2-16), and (2-17) can be written as:

$$Q_N(V,T) = \frac{1}{N!}\int d^3r_1 \cdots d^3r_N \exp\left(-\sum_{i<j} v_{ij}/kT\right) \tag{4-1}$$

$$Z_N(V,T) = (2\pi mkT/h^2)^{3N/2} Q_N \tag{4-2}$$

$$\Xi(z,V,T) = \sum_{N=0}^{\infty} z^N Q_N \tag{4-3}$$

A mathematical trick has been used for calculating the configuration integral Q_N by introducing a function f_{ij} which is defined as:

$$\exp(-v_{ij}/kT) = 1 + f_{ij} \tag{4-4}$$

For the usual type of intermolecular potentials v_{ij} (hard core with finite range attractive interaction), f_{ij} is everywhere bounded and is negligibly small when the distance between the ith and jth molecule is larger than the range of the intermolecular potential. In terms of f_{ij} the configuration integral may be represented as a sum:

$$Q_N(V,T) = \frac{1}{N!}\int d^3r_1 \cdots d^3r_N \prod_{i<j} (1+f_{ij}) \tag{4-5}$$

in which the integral is a product of N(N - 1)/2 terms, one for each distinct pair of particles. Expanding this product we obtain

$$Q_N(V,T) = \frac{1}{N!}\int d^3r_1 \cdots d^3r_N \left[1 + (f_{12}+f_{13}+\cdots) + (f_{12}f_{13}+\cdots) + \cdots\right] \tag{4-6}$$

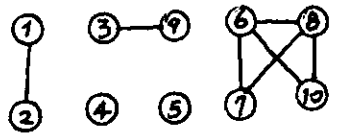
A convenient way to enumerate all the terms in the expansion is to associate each term with a graph, defined as follows: an N-particle graph is a collection of N distinct circles numbered 1, 2, ..., N, with any number of lines joining the same number of distinct pairs of circles. If the distinct pairs joined by lines are the pairs a, b, ..., n, then the graph represents the term

$$\int d^3r_1 \cdots\cdots d^3r_N \, f_a f_b \cdots f_n \tag{4-7}$$

appearing in the expansion Equation (4-6), where the subscripts a, b, ..., n stand for the pairs of molecules. If the set of distinct pairs $\{a, b, \ldots, n\}$ is joined by lines in the given graph, replacing this set by a set $\{a', b', \ldots, n'\}$ that is not identical with $\{a, b, \ldots, n\}$ gives rise to a graph that is counted as distinct from the original one, although the integrals represented by the respective graphs have the same numerical value. For example, for N = 3, the following graphs are distinct:

but the following graphs are identical:

We may express Equation (4-7) by a graph. For example, we may write, for N = 10,



$$= \int d^3r_1 \cdots d^3r_{10} \, f_{12} f_{39} f_{67} f_{68} f_{10\,8} f_{6\,10} f_{78}$$

With such a convention, we can state that

$$Q_N(V,T) = \text{(sum of all distinct N-particle graphs)} \tag{4-8}$$

We introduce next the cluster with ℓ particles (ℓ-cluster and the cluster sums $S_{i,j,k,\ldots}$. An ℓ-cluster is defined to be an ℓ-particle graph in which every circle representing a particle is joined directly or indirectly to all other ℓ-1 circles at least by one line. The cluster sum $S_{i,j,k,\ldots}$ is the sum of all terms which connect in a cluster each of the molecules (circles) i, j, k, ..., no other molecules being connected to this cluster. With these definitions, we define a cluster integral $b_\ell(V,T)$ by

$$\begin{aligned} b_\ell(V,T) &= \frac{1}{\ell! V} \text{ (sum of all possible } \ell\text{-clusters)} \\ &= \frac{1}{\ell! V} \int\cdots\int S_{1,2,\cdots,\ell}\, d^3r_1 \cdots d^3r_\ell \\ &= \frac{1}{\ell! V} \int \sum \Big[\prod_{i<j\le\ell} f_{ij} \Big]\, d^3r_1 \cdots d^3r_\ell \end{aligned} \tag{4-9}$$

Any N-particle graph is a product of a number of clusters, which is characterized by m_1 unit clusters, m_2 clusters of two molecules, ..., m_ℓ of ℓ molecules, with the constraint

$$N = \sum_{\ell=1}^{N} \ell\, m_\ell \tag{4-10}$$

By consideration of : (i) there are m_ℓ ℓ-clusters, and a permutation of these m_ℓ things does not lead to a new graph; (ii) in the sum over

all ℓ-clusters, a permutation of the particles within it does not lead to a new graph, the contribution of a N-particle graph to the Q_N can be written as:

$$\prod_{\ell=1}^{N} \frac{1}{m_\ell!} (V b_\ell)^{m_\ell} \tag{4-11}$$

and hence the configuration integral

$$Q_N(V,T) = \sum_{\{m_\ell\}} \prod_{i=1}^{N} \frac{1}{m_\ell!} (V b_\ell)^{m_\ell} \qquad \left(N = \sum_{\ell=1}^{N} \ell m_\ell\right) \tag{4-12}$$

Substituting into Equations (4-2) and (4-3) we obtain the partition function and grand partition function as follows:

$$Z_N(V,T) = \sum_{\{m_\ell\}} \prod_{\ell=1}^{N} \frac{1}{m_\ell!} (V b_\ell)^{m_\ell} / \Lambda^{3N} \qquad \left(N = \sum_{\ell=1}^{N} \ell m_\ell\right) \tag{4-13}$$

$$\frac{1}{V} \ln \Xi(z, V, T) = \sum_{\ell=1}^{\infty} b^\ell z^\ell \tag{4-14}$$

From which the equation of state can be obtained in parametric form:[34]

$$P/KT = \sum_{\ell=1}^{\infty} b_\ell z^\ell \tag{4-15}$$

$$\rho = \sum_{\ell=1}^{\infty} \ell b_\ell z^\ell \tag{4-16}$$

B. Mayer's Theory of Condensation

Here we do not attempt to go through all the well-known formalism[34] and tedious analysis for Mayer's theory of condensation, but state his conjecture as follows: the condensation point of the system described by b in Equations (4-15) and (4-16) is given by the smallest real positive singularity of the analytic function defined by the power series.

The singularity behavior of the Mayer theory is still a conjecture at the present stage and a lengthy discussion can be found in the article entitled "Singularities in First-Order Phase Transitions" by S. Katsura.[37]

Alternative Derivations for Mayer Theory[38]

In order to understand some insight of Frenkel and Band's approximate theory and Fisher's droplet model, we would like to present this section to link these physical models with the Mayer cluster theory.

A. Maximum Term Method

In this section we try to show that for a system with large N molecules (eventually $N \to \infty$), the equation of state obtained by Mayer can be derived by, mathematically, the 'most probable' method in statistics. In the present case, we try to find a particular set of clusters, say m_l^*, giving the largest term in Equation (4-13). First we write

$$t = \prod_{l=1}^{N} \frac{(Vb_l)^{m_l}}{m_l!} \tag{4-17}$$

and maximize (ln t) with respect to m_l, with the restraint expressed by Equation (4-10).

Using Lagrange's method of undetermined multipliers, we have

$$m_\ell^* = \nu b_\ell s^\ell \qquad \ell = 1, 2, \cdots, N \tag{4-18}$$

where $s = \exp(-\lambda)$, and λ is the undetermined multiplier which can be determined by condition Equation (4-10). Equation (4-18) in Equation (4-10) then gives

$$N = \sum_{\ell=1}^{N} \nu \ell b_\ell s^\ell \tag{4-19}$$

Equation (4-19) determines s as a function of N/V and T.

Now, from Equations (2-14), (4-13) and (4-17)

$$\begin{aligned} F &= -KT \ln Z_N = NKT \ln \Lambda^3 - KT \ln t_{max} \\ &= NKT \ln \Lambda^3 - KT \sum_{\ell=1}^{N} (m_\ell^* \ln \nu b_\ell - m_\ell^* \ln \nu b_\ell s^\ell + m_\ell^*) \\ &= NKT \ln \Lambda^3 + NKT \ln s - KT \sum_{\ell=1}^{N} m_\ell^* \end{aligned} \tag{4-20}$$

Since the Helmholtz free energy $F = \mu N - PV$, and $F = -kT \ln Z_N$

$$\begin{aligned} -\mu/KT &= \left(\frac{\partial \ln Z_N}{\partial N}\right)_{V,T} \\ &= -\ln \Lambda^3 - \ln s - \frac{N}{s}\frac{\partial s}{\partial N} + \sum_{\ell=1}^{N} \nu \ell b_\ell s^{\ell-1} \frac{\partial s}{\partial N} \\ &= -\ln \Lambda^3 - \ln s \end{aligned} \tag{4-21}$$

From Equations (4-21) and (2-18) we conclude that s is just the activity z. Equations (4-21) and (4-20) give

$$PV/KT = \sum_{\ell=1}^{\infty} m_\ell^* = \sum_{\ell=1}^{\infty} \nu b_\ell z^\ell \tag{4-22}$$

which gives Equation (4-15) in the limit $N \to \infty$.

B. Association Equilibrium for Mathematical Cluster

Fowler[38] pointed out that imperfect theory can be treated as a problem in dissociation. In a formal way, we can consider that the imperfect gas is a perfect gas mixture of different species in equilibrium with each other. In the processes of association and dissociation the clusters may change their composition but at equilibrium there is a certain mean number $\bar{N}_\ell$ of clusters of size ℓ . With this consideration, we can write Equation (4-13) in a form as follows:

$$Z_N(V,T) = \prod_{\ell=1}^{N} \Omega_\ell \tag{4-23}$$

where $\Omega_\ell = \dfrac{q_\ell^{\bar{N}_\ell}}{\bar{N}_\ell}$ and $q_\ell = \dfrac{V b_\ell}{\Lambda^{3\ell}}$ (4-24)

is the partition function for the $\bar{N}_\ell$ clusters of size ℓ and q_ℓ is the partition function per cluster for clusters of size ℓ . The condition for association equilibrium in a gas mixture is governed by the mass action law[38]

$$\bar{N}_1^{\ell} / \bar{N}_\ell = q_1^{\ell} / q_\ell \tag{4-25}$$

Now the chemical potentials of clusters of size ℓ are given by

$$-\mu_\ell / kT = \left(\frac{\partial \ln \Omega_\ell}{\partial \bar{N}_\ell}\right)_{V,T} = \ln q_\ell - \ln \bar{N}_\ell \tag{4-26}$$

Substituting Equation (4-25) into (4-26) we have

$$-\mu_\ell / kT = \ln q_\ell - \ln \bar{N}_\ell = \ell (\ln q_1 - \ln \bar{N}_1) = -\frac{\ell \mu_1}{kT} \tag{4-27}$$

From Equations (4-26) and (4-27), we obtain the mean number $\bar{N}_l$ of clusters of size l

$$\bar{N}_l = q_l e^{-\mu_l/kT} = q_l e^{-l\mu_1/kT}$$
$$= \frac{V b_l}{\Lambda^{3l}} e^{-l\mu_1/kT} \qquad (4\text{-}28)$$
$$= V b_l z^l$$

where we have defined z by Equation (2-18). $\left(z = \frac{e^{\mu_1/kT}}{\Lambda^3} \right)$

The partial pressure p_l due to clusters of size l is

$$p_l = kT \left(\frac{\partial \ln \Omega_l}{\partial V} \right)_{\bar{N}_l, T} = \frac{\bar{N}_l kT}{V} \qquad (4\text{-}29)$$

and

$$\frac{pV}{kT} = \sum_{l=1}^{N} \frac{p_l V}{kT} = \sum_{l=1}^{N} \bar{N}_l \qquad (4\text{-}30)$$

or

$$\frac{p}{kT} = \sum_{l=1}^{N} b_l z^l$$

Hence, the same expression for the equation of state is arrived. We notice that, with mathematical expression, the mean number $\bar{N}_l$ of clusters of size l for the association equilibrium in a perfect gas mixture is exactly equal to the most probable value we have derived in Section A. However, the analogy with an actual equilibrium between physical clusters is limited. (The b_l can be negative for some calculations.[38])

Frenkel[35] and Band[36] Droplet Model

Frenkel and Band in 1939 independently pointed out that an approximate theory very analogous to Mayer's could be developed, based upon the equilibrium association of physical clusters. In Section B, we have seen

that Mayer's result can be obtained by constructing mathematical clusters with the assumption of association equilibrium for a perfect-gas mixture of clusters. However, the mathematical clusters cannot be identified directly with the physical clusters without any physical justification. In this section we will describe the droplet model introduced by Frenkel and Band which provides a crude connection with the Mayer's theory. Although the ideas are quite straightforward, the stimulus of their work seems to have come from Mayer's work but avoiding the rigorous and tedious expansion for the cluster integrals. We shall give their droplet model as follows: in an imperfect gas there exists clusters of various sizes and between these clusters there is an association-dissociation equilibrium and no interaction among them. For sufficient large clusters, the clusters will actually behave as small liquid droplets, and these droplets with ℓ molecules can be treated as a single 'molecule' with mass ℓm, where m is a molecule mass. With this physical picture, the partition function for the cluster of size ℓ, say J_ℓ , can be approximately written as:

$$J_\ell = \frac{V}{\Lambda'^3} \exp\left(-\frac{\Phi}{KT}\right) \quad ; \quad \Lambda' = \left(\frac{h^2}{2\pi \ell m KT}\right)^{\frac{1}{2}}$$

where Φ is the potential energy of such a not too small cluster of molecules, which may be decomposed into a bulk term, determined by the binding energy per molecule in the liquid, say E_o, and a remainder W which is associated with the loss of binding energy at the 'surface' of the cluster. For large clusters W can be approximated by $c\,\ell^{2/3}$, where c is a constant proportional to the surface tension, J_1, the partition function for one molecule is V/Λ^3. (The potential energy in this case

is zero, and $\Lambda = \left(\frac{h^2}{2\pi m KT}\right)^{\frac{1}{2}}$.

By replacing the physical cluster partition function J_ℓ for the mathematical cluster partition function q_ℓ in Equations (4-24) and (4-28) and with Equation (4-30), we obtain the equation of state for N

$$P/KT = \frac{1}{\Lambda^3} \sum_{\ell=1}^{\infty} \ell^{3/2}\, \bar{x}^{\ell^{2/3}}\, \bar{y}^{\ell} \tag{4-31}$$

Hence, the density of the system

$$\rho = \frac{1}{\Lambda^3} \sum_{\ell=1}^{\infty} \ell^{5/2}\, \bar{x}^{\ell^{2/3}}\, \bar{y}^{\ell} \tag{4-32}$$

where

$$\bar{x} = \exp\left(-c/KT\right) \tag{4-33}$$

$$\bar{y} = \exp -\left(\mu - E_0\right)/KT \tag{4-34}$$

Fisher's Modified Droplet Model[10]

Without detailed discussion, we can simply summarize Fisher's modified droplet model in the following fashion: the equation of state for an infinite system can be written as:

$$P/KT = \mathcal{G}_0 \sum_{\ell=1}^{\infty} \ell^{-\tau}\, x^{\ell^{\sigma}}\, y^{\ell} \tag{4-35}$$

$$\rho = \mathcal{G}_0 \sum_{\ell=1}^{\infty} \ell^{1-\tau}\, x^{\ell^{\sigma}}\, y^{\ell} \tag{4-36}$$

where

$$x = \exp\left[a_0 (W - \omega T)/KT\right] \tag{4-37}$$

and

$$y/\bar{z} = \exp\left[E_o/\kappa T + S_o/\kappa \right] \tag{4-38}$$

Here w = microscopic surface energy arising through loss of binding energy by particles near the surface of the cluster, ω= corresponding entropy per unit cluster surface area, $\bar{z} = \exp(\mu/kT)$, E_0 = bulk energy per particle in the cluster, S_0 = bulk entropy per particle in the cluster, a_o is a proportionality constant due to the assumption that the most probable surface area for the cluster with ℓ molecules equals to $a_o \ell^{\sigma}$; g_o and τ are new fitting parameters based on heuristic arguments related to the combinatorial questions of excluded-volume problem.[10] By comparing the equation of state derived by Frenkel and Band with Equations (4-35) and (4-36), it is not hard to see that the only modification is merely replacing the fixed constants, such as Λ^3, power of ℓ etc. of Frenkel Band theory with parameters, g_o, τ and σ. However, this little change reveals very significant information for phenomena near the critical region. We shall proceed to a discussion of this in the next section.

Cluster Theory and Critical Phenomena

In characterizing the behavior of thermodynamic equilibrium properties, besides the conditions for thermodynamic stability and the analyticity of the equation of state, the critical exponents has been introduced recently[5] as an another powerful tool. Critical exponents have usually served as the common meeting ground between theory and experiment, whose applications and definitions have been shown in the last two chapters. Here again we will use this additional tool for our analysis of the critical phenomena for the cluster theory.

A. Mayer's Theory and Critical Phenomena

For more than thirty years, the critical phenomena of Mayer's theory has been considered as one of the most basic and yet difficult problems in statistical mechanics. An essential difficulty of Mayer's theory is the treatment of the cluster integral b_l. Difficulties in connection with the double limiting process of the equation of state ($P/kT = \lim_{V\to\infty} \sum_{l\geq 1} b_l (V,T) z^l$), convergence of $\sum_{l\geq 1} b_l (V,T) z^l$, volume dependence of the cluster integrals, etc. arise when one attempts to include condensation, the critical point, and the liquid phase.[38] Here we do not attempt to go through all the well-known formalism and tedious analysis for Mayer's theory of condensation; however, we will quote the conclusions drawn by Yang and Lee[6] after a rigorous mathematical analysis as follows:

1. Throughout the gas phase Mayer's theory gives correct results.

2. For $\rho \geq \rho_1$ (ρ_1 is given by the smallest real positive singularity of the analytical function defined by the power series $\sum_{l\geq 1} b_l(V,T) z^l$)

   Mayer's conclusion that the p-V diagram becomes horizontal is incorrect due to the existence of the liquid phase. It is not even justified for densities immediately above ρ_1, as for transitions of high order the isotherm does not even have any horizontal part at all.

The conclusion is clearly indicated that Mayer's theory is inadequate for the critical point and liquid phase. But there has been no analysis which gives an indication of how well Mayer's theory can reproduce equilibrium behavior in the gas phase and very near to the critical region. This in turn means that thereis not answer to the question, "What are the so-called critical exponents for Mayer's theory in the gas

phase?" We will attempt to answer this question partially in the following fashion: Mayer and Harrison[34] have shown that for large ℓ, the cluster integral b_ℓ can be written as

$$b_\ell = f_b(\ell)\, b_o^{\ell}(T) \tag{4-39}$$

where

$$f_b(\ell) = \rho_o \Big/ \left[\left(2\pi \sum_{\kappa=1}^{\ell} \kappa^2 \beta_\kappa \rho_o^{\kappa} \right)^{\frac{1}{2}} \ell^{5/2} \right] \tag{4-40}$$

$$b_o(T) = \left(\exp \sum_{\kappa=1}^{\ell} \beta_\kappa \rho_o^{\kappa} \right) \Big/ \rho_o \tag{4-41}$$

β_K is the irreducible cluster integral, ρ_o defined by $\sum_{\kappa=1}^{\ell} \kappa \beta_\kappa \rho_o^{\kappa} = 1$.[39] They also have shown that $\sum_{\kappa=1}^{\ell} \kappa^2 \beta_\kappa \rho_o^{\kappa}$ increases with ℓ, therefore $f_b(\ell)$ will decrease more rapidly with ℓ than as $1/\ell^{5/2}$. With these results of Mayer and Harrison, we can write down the equation of state for large ℓ,

$$\pi(T, z) = \frac{P}{\kappa T} = \frac{1}{\Lambda^{3N}} \sum_{\ell=1}^{\infty} f_b(\ell)\, b_o^{\ell}(T)\, z^{\ell} \tag{4-42}$$

$$\rho = z \frac{\partial \pi}{\partial z} = \pi^{(1)}(T, z) = \frac{1}{\Lambda^{3N}} \sum_{\ell=1}^{\infty} \ell\, f_b(\ell)\, b_o^{\ell}(T)\, z^{\ell} \tag{4-43}$$

$$\kappa T^2 K_T = \pi^{(2)}(T, z) = \frac{1}{\Lambda^{3N}} \sum_{\ell=1}^{\infty} \ell^2 f_b(\ell)\, b_o^{\ell}(T)\, z^{\ell} \tag{4-44}$$

. . . . . .

$$\pi^{(n)}(T, z) = \frac{1}{\Lambda^{3N}} \sum_{\ell=1}^{\infty} \ell^n f_b(\ell)\, b_o^{\ell}(T)\, z^{\ell} \tag{4-45}$$

If $f_b(\ell)$ were proportional to $1/\ell^{5/2}$ for large ℓ, Equation (4-45) could be approximated as:

$$\pi^{(n)}(T,z) \sim \int_1^\infty \ell^{n-5/2} \exp\{\ell \ln(b_o z)\} d\ell$$

$$\sim \int_1^\infty \ell^{n-5/2} \exp\{-\ell(1-b_o z)\} d\ell$$

$$= \Gamma(n+1-5/2,\ 1-b_o z) \Big/ (1-b_o z)^{n+1-5/2}$$

(4-46)

where $\Gamma(n+1-5/2, 1-b_o z)$ is an incomplete Gamma function.[46]

With this expression we are able to relate the critical exponents and Mayer's cluster theory. In general this expression agrees with the analysis from the analytical argument which states that when $z \sim b_o^{-1}$, some singularity behavior appears.[34] As indicated in Equation (4-46), the compressibility will approach infinite (n = 2), and for $b_o z < 1$, all the thermodynamic functions behave well. However, the same problem exists as before, that is "how to determine explicitly the $f_b(\ell)$ and $b_o(T)$?" Nevertheless, we are certain that both quantities are playing an extremely important role near the critical point, and from our analysis, $f_b(\ell)$ must be a decreasing function of ℓ, and will not decrease more rapid than $1/\ell^3$, or the compressibility will not approach infinity at the critical point.

B. Liquid Droplet Model and Critical Phenomena[10]

Although Fishers' droplet model was not derived rigorously from the statistical theory, and certain parameters, e.g. the parameter τ, do not have any real clear physical significance, a tremendous information

is revealed near the critical point with the help of the powerful tool-critical exponents. Therefore we would like to introduce Fishers' analysis for his model near the critical point, and apply his analysis for Frenkel and Band's droplet model and Mayer's theory.

Condensation. Consider the probability of finding a cluster of size ℓ which is proportional to m^*_ℓ . From Equations (4-22) and (4-35), we notice that this probability is proportional to ρ_ℓ where

$$\rho_\ell = \xi_0 \, x^{\ell^\sigma} y^\ell / \ell^\tau \tag{4-47}$$

At low temperature x is small (see Equation (4-41)) and at low activities (z) (and hence low density) y is also small. In this case, ρ_ℓ decays rapidly to zero as ℓ increases. As y approaches unity the decay becomes slower. On the other hand, when y is slightly larger than unity the probability at first decreases because of the factor x^{ℓ^σ} but eventually increases when the exponent-$|(\ln y)|\ell^\sigma$ dominates the exponent - $|\ln x|\ell^\sigma$. The large probability (divergent) of large clusters indicates that condensation has taken place. Consequently we identify y = 1 as the condensation point. Hence we can find the chemical potential at the condensation. By the same token, we can determine the critical temperature by letting x = 1. From Equation (4-37) this means $T_c = \omega/w$ (at the critical point the surface tension for a cluster will vanish). Therefore the critical pressure and density can be determined as: (see Equations (4-39) and (4-40)

$$P_c/\kappa T_c = \xi_0 \sum_{\ell=1}^{\infty} \ell^{-\tau} = \zeta(\tau)\xi_0 \tag{4-48}$$

$$\rho_c = \xi_0 \sum_{\ell=1}^{\infty} \ell^{1-\tau} = \xi_0 \zeta(\tau-1) \tag{4-49}$$

where $\zeta(x)$ is a Zeta function of x.

Analytic Character and the Critical Exponents. For fixed temperature, and hence fixed x, the radius of convergence of the series Equation (4-39) is given by

$$y_0 = \lim_{\ell \to \infty} |\ell^{-\tau} x^{\ell^\sigma}|^{-1/\ell} = \lim_{\ell \to \infty} |x|^{-1/\ell^{1-\sigma}} = 1 \tag{4-50}$$

for all x.

The last equality follows from the assumption $\sigma < 1$. Since the terms in Equation (4-39) are positive the point $y_0 = 1$ must be a singularity of the function, P/RT. Furthermore, $y_0 = 1$ coincides with the condensation point y = 1 as described above. For this model, Mayer's theory is verified. (See Section IV-B)

Also, (see Equation (4-45))

$$\begin{aligned} \Pi^{(n)}(T, z) &= (z\partial/\partial z)^n \Pi \\ &= \xi_0 \sum_{\ell=1}^{\infty} \ell^{n-\tau} x^{\ell^\sigma} y^\ell \end{aligned} \tag{4-51}$$

(n) denotes the nth derivatives.

At the condensation point we find

$$\Pi_\sigma^{(n)}(T) = \xi_0 \sum_{\ell=1}^{\infty} \ell^{n-\tau} x^{\ell^\sigma} \tag{4-52}$$

denotes, at the condensation, y = 1.

This series converges for all n provided only x 1. The fact that

all the derivatives with respect to z remain finite at the $z = z_\sigma$, even though we have established that this is a singularity of $\pi(z)$, indicates the singularity at $z = z_\sigma$ is an essential singularity of $\pi(z)$.

To derive the critical exponents for the droplet model, we can start from Equation (4-50) with the approximation

$$\pi_\sigma^{(n)}(T) = \delta_0 \int \ell^{n-\tau} \exp\left[-(\ln x^{-1})\ell^\sigma\right] d\ell \qquad (4\text{-}53)$$

and change the variable $t = \theta \ell^\sigma$, where

$$\theta = \ln x^{-1} = \frac{2\omega}{kT}(T_c - T) \qquad (4\text{-}54)$$

yields

$$\pi_\sigma^{(n)}(T) \simeq (\delta_0/\sigma\theta^{(n-\tau+1)/\sigma})\,\Gamma\left(\frac{n-\tau+1}{\sigma}\right) \qquad (4\text{-}55)$$

where $\Gamma(x)$ is a Gamma function of x.

Since

$$\rho(T, z) = \pi^{(1)}(T, z) \qquad (4\text{-}56)$$

and

$$kT\rho^2 K_T = \pi^{(2)}(T, z) \qquad (4\text{-}57)$$

and with the definitions in Chapter II, we obtain

$$\beta = \frac{\tau - 2}{\sigma} \qquad (4\text{-}58)$$

$$\gamma' = \frac{3 - \tau}{\sigma} \qquad (4\text{-}59)$$

The specific heat at constant critical density, which derives from $P_\sigma(T)$,

diverges as

$$\alpha = 2 - \frac{\tau - 1}{\sigma} \tag{4-60}$$

The critical exponent for the critical isotherm (x = 1) will be

$$\delta = \frac{1}{\tau - 2} \tag{4-61}$$

Equations (4-58), (4-59), (4-60), and (4-61) indicate the critical exponents satisfy the equalities conjectures by Widom and Fisher (Equations (2-31) and (2-32).

From experimental measurements the critical exponents β and γ are positive values, therefore the critical parameter τ is restricted as $2 < \tau < 3$ near the critical point.

C. Frenkel-Band's Droplet Model and Critical Phenomena

Comparing Equations (4-31) and (4-35), we notice that a tremendous similarity exists between Frenkel-Band and Fisher's droplet model. Therefore, the same analysis can be applied for Frenkel-Band's approximate cluster theory. However, in Frenkel-Band's model the corresponding critical parameters $\tau = -3/2$ and $\sigma = 2/3$. From these two parameters we obtain all the critical exponents as $\delta = -2/7$, $\beta = -21/4$, $\gamma = 27/4$, and $\alpha = 23/4$. It is obvious that these values for the critical exponents cannot explain any kind of 'critical phenomena'. With the analysis in the end of the section IV-A, where $f_b(\ell)$ must be a decreasing function of ℓ, we are not surprised that the Frenkel and Band's model is inadequate for the critical phenomena with their $f_b(\ell) \sim \ell^{2/3}$. We notice that this $\ell^{2/3}$ term originally comes from the contribution of the momentum space to the partition function for the cluster of size ℓ (see Equation (4-31)). Therefore, it is not hard for us to draw the conclusion that the assumption of 'the droplet

with ℓ molecules can be treated as a single 'molecule' with mass ℓm' has been taken too seriously, which in turn means the contribution of the momentum space is far less than their assumption.

CHAPTER V

HOMOGENEOUS ARGUMENT FOR THE EQUATION OF STATE NEAR THE CRITICAL POINT

From the discussions given in the last two chapters, we have concluded that the conventional analysis of equilibrium properties near the critical point, which utilize the conditions for thermodynamic stability and analyticity of the equation of state, does not give sufficient information for the phenomena near the critical region. The additional tool--critical exponents--seems to have an important role for differentiating the so-called 'classical' and 'non-classical' approaches. The van der Waals type of equation of state has been considered as 'classical' approach simply because the result of the critical exponents predicted by the model cannot explain the experimental data. The Ising model and Fisher's droplet model which both offer some insight into magnitudes and inter-relations of the critical exponents are generally considered as 'non-classical' approaches. In this chapter we will discuss a more phenomenological macroscopic approach which will show why the critical exponents and their relations are useful. This phenomenological macroscopic model-independent approach is generally known as 'homogeneous argument of equation of state near the critical point' or 'scaling assumption for the equation of state near the critical region.'

Homogeneous Argument of Equation of State Near the Critical Point

In 1965, a specific form was proposed by B. Widom[9] for the equation of state of a fluid near the critical point. A function Φ was introduced which is a function of two variables, one a measure of the density of the system and the other a measure of the temperature. It was suggested that in a real fluid of finite dimensionality, the equation of state near the critical point is characterized by Φ being a homogeneous function of its variables, with a positive degree of homogeneity, and analytic in the one phase region. It is just this assumption which leads to the non-classical thermodynamic behavior near the critical region. Fluids obeying an equation of state of van der Waals type are characterized by Φ being a constant.

A. Equation of State

The following equation is the proposed form of the equation of state in one phase region near the critical point:

$$\mu(\rho, T) - \mu(\rho_c, T) = \Delta\rho\ (t + y)\ \Phi(t, y) \qquad (5\text{-}1)$$

where $\Delta\rho = (\rho - \rho_c)/\rho_c$, $t = (T - T_c)/T_c$, $y = 1 - \frac{\tau(\rho)}{T_c}$, $T = \tau(\rho)$ is the equation of the coexistence curve in the T, ρ plane. (The critical isochore, $\rho = \rho_c$, in the μ, T plane, and one general isochore, are shown schematically in Figure 5-1. The general isochore corresponding to density ρ intersects the critical isochore at the temperature $\tau(\rho)$ where $T = \tau(\rho)$. The equation of the coexistence curve in the T, ρ plane is shown in Figure 5-2. The diagram for the chemical potential vs. density near the critical point is shown in Figure 5-3. The Equation (5-1) provides the necessary features of the equation of state near the critical point that the chemical potential reduces to $\mu(\rho_c, T)$ both when $\rho = \rho_c$ and $T = \tau(\rho)$ (below the

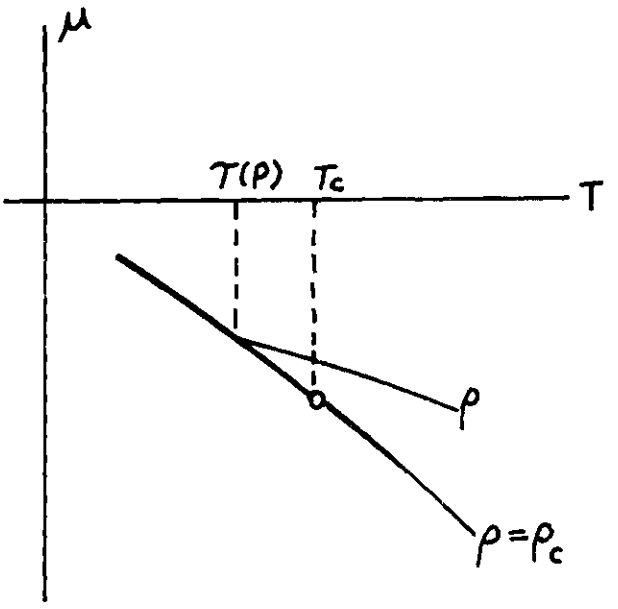


Figure 5-1. The Critical Isochore and a General Isochore in the μ-T Plane

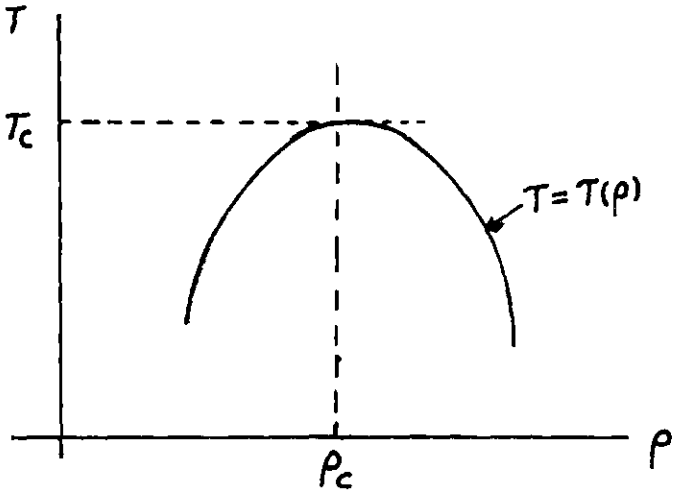


Figure 5-2. The Coexistence Curve $T = \tau(\rho)$ in the T-ρ Plane

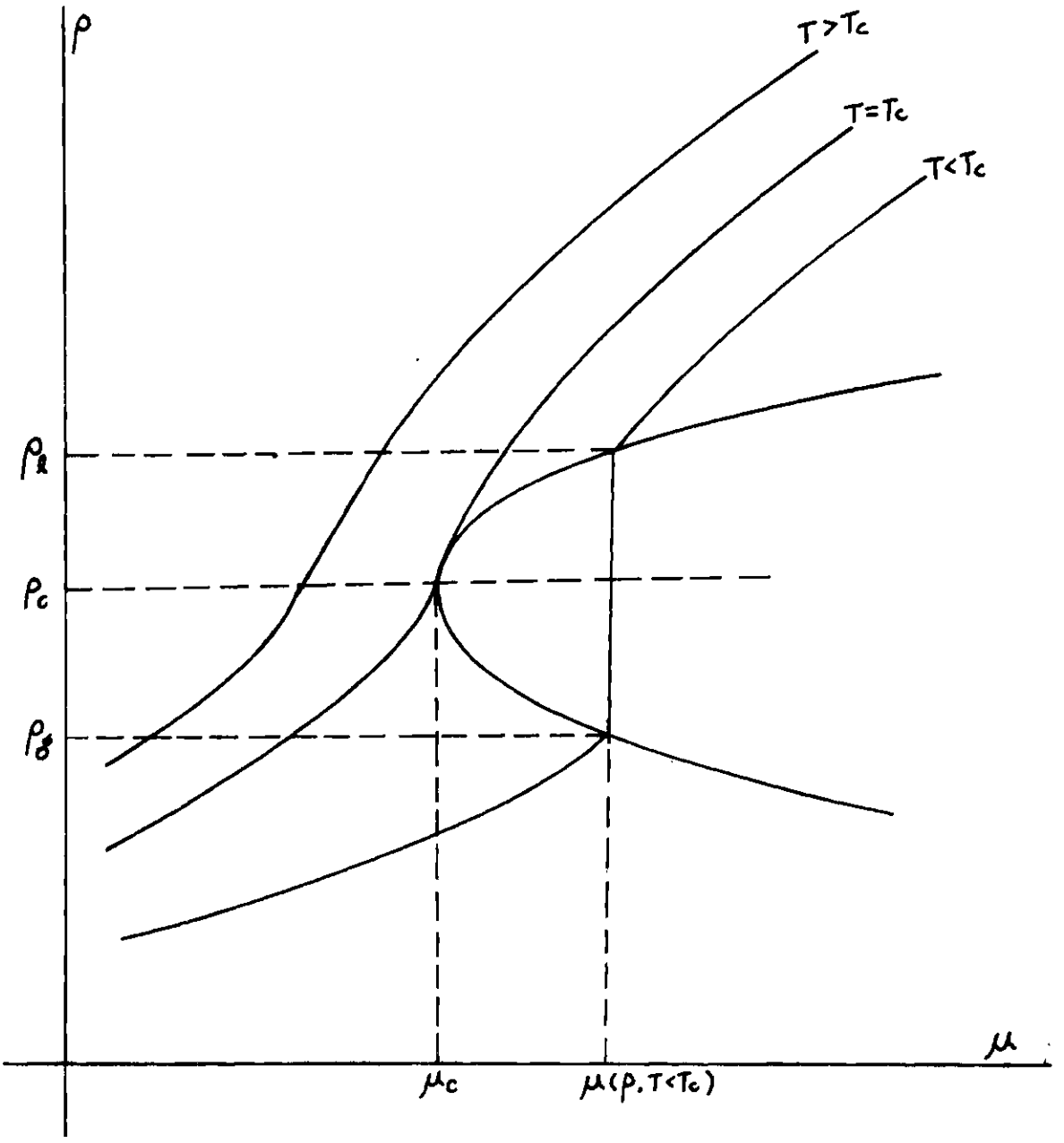


Figure 5-3. Isotherms in the ρ-μ Plane

critical temperature and along the coexistence curve $\mu(\rho_g, T) = \mu(\rho_\ell, T) = \mu(\rho_c, T)$ (See Figures 5-1, 5-2, and 5-3.) With the assumption that Φ is a homogeneous function of its variables with a positive degree of homogeneity, say $(\gamma - 1)$, then what is being conjectured by Widom is that

$$\begin{aligned} \Phi(t, y) &= y^{\gamma-1}\, \Phi(t/y, 1) \\ &= t^{\gamma-1}\, \Phi(1, y/t) \qquad t > 0 \\ &= (-t)^{\gamma-1}\, \Phi(-1, y/-t) \qquad t < 0 \end{aligned} \tag{5-2}$$

with the assumption that $[\mu(\rho, T) - \mu(\rho_c, T)]$ is an analytic function of both density and temperature in the one phase region.

B. Thermodynamic Behavior near the Critical Point

Coexistence Curve. From II-C and Figure 5-2, approaching the critical temperature from below, the coexistence curve can be written as the following:

$$T_c - T(\rho) = \bar{B}\, |\Delta\rho|^{\frac{1}{\beta}} \tag{5-3}$$

Notice that $y = \bar{B}/T_c\, |\Delta\rho|^{\frac{1}{\beta}}$ is a quantity which measures the density.

Compressibility. The isothermal compressibility K_T is defined as

$$K_T = \frac{1}{V} \frac{\partial V}{\partial P}\Big)_T$$

and can be related as $(\rho^2 K_T)^{-1} = \rho^{-1} \left(\frac{\partial \rho}{\partial P}\right)_T = \left(\frac{\partial \mu}{\partial \rho}\right)_T$.

From the coexistence curve and the equation of state, Equations (5-1) and (5-2), with the positive homogeneity $(\gamma-1)$ for $\Phi(t, y)$, we find

(i) on the critical isochore $(\Delta\rho = 0,\ t > 0)$

$$\partial\mu/\partial\rho)_T = \frac{1}{\rho_c}\, t^{\gamma}\, \Phi(1, 0) \tag{5-4}$$

(ii) on the critical isotherm (t = 0)

$$\partial\mu/\partial\rho)_T = \frac{(1+\gamma/\beta)}{\rho_c}\,\Phi(0,1)\,y^{\gamma} \tag{5-5}$$

(iii) at the coexistence curve (t + y = 0)

$$\partial\mu/\partial\rho)_T = \frac{1}{\beta}\,\Phi(1,-1)\,y^{\gamma} = \frac{1}{\beta}\,\Phi(-1,1)(-t)^{\gamma} \tag{5-6}$$

From the definitions of the isothermal compressibility and t, it is seen that the isothermal compressibility becomes infinite proportional to $|T-T_c|^{-\gamma}$ as the critical point is approached along either the critical isochore or the coexistence curve. With $\gamma > 1$, that is with the degree of homogeneity (γ - 1) assumed positive, this is just the non-classical behavior of the compressibility which is found in real systems. (γ = 1 is the classical result.) It is not hard to see for Φ, a constant, the critical exponent γ equals 1.

Critical Isotherm. For the critical isotherm, t = 0, the equation of state (5-1) can be written as:

$$\Delta\mu = \mu(\rho,T) - \mu(\rho_c,T) = \Phi(0,1)\,\Delta\rho\,y^{\gamma}$$
$$= \Phi(0,1)\,\Delta\rho\,|\Delta\rho|^{\gamma/\beta} \tag{5-7}$$

Since the critical exponent for the critical isotherm is defined as δ, therefore the equality conjectured by Widom is satisfied (see Equation (2-31).

Constant-volume Specific Heat on the Critical Isochore. As we noticed in Chapter II, the equation of state expressed in the form of Equation (5-1) is not a fundamental relation and does not contain all

possible thermodynamic information about the system. In fact the present equation of state actually is a partial differential equation of the free energy. Even if this equation were integrable, it would yield a fundamental equation with undetermined functions. To find the specific heat at constant volume from Equation (5-1), we have to integrate the present equation of state with respect to the density to get the free energy F and then obtain the specific heat. ($C_V = -T\frac{\partial^2 F}{\partial T^2}$) Here we do not go through the details to give an explicit form for the specific heat at constant volume, but discuss the singularity behavior near the critical point.

From Equation (5-7) we notice that the chemical potential near the critical point is proportional to $\Delta\rho^{1+\gamma/\beta}$. After we integrate the equation of state with respect to density, we have the free energy which will be proportional to $\Delta\rho^{\gamma/\beta+2}$ or $t^{\gamma+2\beta}$ near the critical point (see Equation (5-20)). By taking the second derivative with respect to temperature, we obtain the exponent for the specific heat at constant volume which is $\gamma+2\beta-2$. Together with the definition of the specific heat at constant volume near the critical point the equality $\alpha=\gamma+2\beta-2$, conjectured by Fisher (see Equation (2-32)) is arrived.

Scaling Assumption for the Equation of State Near the Critical Point

In 1967, Griffiths[9] adopted Widom's homogeneous argument and proposed an equation of state near the critical point in magnetic language, in which the homogeneous function Φ was replaced by a function h(x) of dimensionless quantities with appropriate combination of critical parameters. Even though it is a disguised form of Widom's expression,

the proposed equation of state by Griffiths does give simpler expressions and clearly defines conditions on h(x). Hence, it is often used by the experimentalists to confirm the scaling ideas near the critical region.

A. Equation of State

As we mentioned above, Griffiths has proposed an equation of state near the critical point in terms of magnetic language. The magnetic equation of state can be written as:

$$H(M,T) = M\,|M|^{\delta-1}\,h(x) \qquad (5\text{-}8)$$

near the critical point, where M is the spontaneous magnetization, $x = t/|M|^{1/\beta}$ and $t = (T - T_c)/T_c$. h(x) is analytic in its range of definition, $-x_o < x < \infty$, equals 0 at $x = -x_o$, the coexistence curve ($M = B(-t)^{\beta}$ for $t < 0$, therefore x_o is defined as $B^{-1/\beta}$) and possesses series expansions.

$$h(x) = \sum_{n=1}^{\infty} \eta_n x^{\beta(\delta+1-2n)} \qquad \text{for large x} \qquad (5\text{-}9)$$

$$h(x) = \sum_{n=1}^{\infty} \xi_n x^{n} \qquad \text{for small x} \qquad (5\text{-}10)$$

so that H is analytic in t and M across the critical 'isochore' (H = 0) for all $t > 0$.

Using the transformation role given in Chapter III, the equation of state can be written for fluids as:

$$\Delta\mu = \mu(\rho,t) - \mu(\rho_c,t) = \Delta\rho\,|\Delta\rho|^{\delta-1}\,h_F(\bar{x}) \qquad (5\text{-}11)$$

with $\bar{x} = t/|\Delta\rho|^{1/\beta}$, $\Delta\rho = (\rho-\rho_c)/\rho_c$, and $t = (T - T_c)/T_c$. The connection between Equations (5-11) and (5-1) is given later.

B. Thermodynamic Behavior near the Critical Point

Susceptibility (Compressibility in Fluids). With Equation (5-8) and definition of the isothermal susceptibility we have

$$\left(\partial H/\partial M\right)_T = \chi^{-1} = M^{\delta-1}\,\delta\, h(x) - \beta^{-1} x\, h'(x)$$
$$= t^{\beta(\delta-1)}\left[\delta h(x) - \beta^{-1} x h'(x)\right]/x^{\beta(\delta-1)} . \qquad (5\text{-}12)$$

Hence,

(i) on the critical isochore (H = 0; and for t > 0)

$$\chi^{-1} = t^{\beta(\delta-1)} \lim_{x\to\infty} \frac{\left[\delta h(x) - \beta^{-1} x h'(x)\right]}{x^{\beta(\delta-1)}} . \qquad (5\text{-}13)$$

(ii) on the coexistence curve ($x = -x_o$) ($h(-x_o) = 0$)

$$\chi^{-1} = t^{\beta(\delta-1)} \frac{h'(-x_o)}{\beta\, x_o^{\beta(\delta-1)-1}} . \qquad (5\text{-}14)$$

The critical exponent for the isothermal susceptibility is γ, and from Equations (5-13) and (5-14) we obtain the equality (see Equation (2-31)) $\gamma = \beta(\delta-1)$ once again.

Critical Isotherm (t = 0, i.e. x = 0). From the equation of state, (5-8), we obtain

$$H(M, T_c) = M^{\delta} h(0) \qquad \text{along the critical isotherm} \qquad (5\text{-}15)$$

Specific Heat at Constant M on H = 0. We have the same problem here as encountered in Widom's analysis, that the free energy is not known. However, Griffiths has assumed the free energy has the following form:

$$A(M,T) = A_o(T) + |M|^{\delta+1}\, a(t\,|M|^{-1/\beta}) \qquad (5\text{-}16)$$

in the one phase region, with $A_o(T)$ and analytic function of the temperature and a(x) satisfying the differential equation:

$$-x\,a'(x) + \beta(\delta+1)\,a(x) = \beta\,h(x) \tag{5-17}$$

By solving this differential equation, we obtain the free energy as a function derivable from the equation of state, Equation (5-8). The general solution of Equation (5-17) may be written as

$$a(x) = C\,x^{\beta(\delta+1)} + \beta x^{\beta(\delta+1)} \int^{x} h(y)\, y^{-[\beta(\delta+1)+1]}\, dy \tag{5-18}$$

Substituting Equation (5-18) into Equation (5-16), we get

$$A(M,T) = A_0(T) + t^{\beta(\delta+1)} \left(C + \beta \int^{x} h(y)\, y^{-[\beta(\delta+1)+1]}\, dy \right) \tag{5-19}$$

Near H = 0, i.e. for large x, with Equation (5-9), we have

$$A(M,T) = A_0(T) + t^{\beta(\delta+1)} \left(C + \frac{1}{2} \sum_{n=1}^{\infty} n^{-1} \eta_n x^{-2\beta n} \right) \tag{5-20}$$

With this expression, we can prove easily the equality given in Equation (2-30) for the critical exponents, by taking the second temperature derivative

$$-\alpha = \beta(\delta+1) - 2 \qquad \text{or} \qquad 2 = \beta(\delta+1) + \alpha$$
$$= \gamma + 2\beta + \alpha$$

The Equivalence Between Widom and Griffiths' Equation of State Near the Critical Point

Widom's equation of state (Equation (5-1)) can be written as:

$$\Delta\mu = \Delta\rho\,(t+y)\,y^{\gamma-1}\,\Phi(t/y, 1)$$
$$\simeq \Delta\rho\,(1 + t/y)\,y^{\gamma}\,\Phi(t/y, 1)$$

where $y = \bar{\beta}/T_c |\Delta\rho|^{\frac{1}{\beta}}$

Let $x = t/y'$ and with $\gamma = \beta(\delta-1)$

$$\Delta\mu \sim \Delta\rho\,|\Delta\rho|^{\delta-1}(1+x)\,\Phi(x,1)$$
$$\simeq \Delta\rho\,|\Delta\rho|^{\delta-1}\,h(x) \qquad (5\text{-}21)$$

where $h(x) = (1 + x)\,\Phi(x,1)$.

Where Equation (5-21) is the equation of state proposed by Griffiths (see Equation (5-11)).

Different Expression for the Equation of State Near the Critical Point

In this section we utilize the scaling ideas proposed by Widom and Griffiths and propose different expressions for the equation of state near the critical point.

We assume the equation of state near the critical point in the following form:

$$\Delta\mu = (\mu_c - \mu)/kT = \Delta\rho(t + |\Delta\rho|^{1/\beta})\,\Phi_1(t, |\Delta\rho|^{1/\beta}) \qquad (5\text{-}22)$$

and

$$\Delta\mu = t\,(|\Delta\rho| + t^{\beta})\,\Phi_2(|\Delta\rho|, t^{\beta}) \qquad (5\text{-}23)$$

where Φ_1, Φ_2 are homogeneous functions of their variables with γ-1 degrees of homogeneity and $\Delta\mu$ is analytic in $\Delta\rho$ and t in the one phase region. The rest of the notations have been defined before.

The obvious difference between this equation of state and the one proposed by Widom is the definition of $\Delta\mu$. With his assumption,

$\Delta\mu = \mu(\rho,T) - \mu(\rho_c,T)$, $\Delta\mu$ equals 0 either along the coexistence curve or $\rho \to \rho_c$. In this present proposed form, we allow $\Delta\mu$ equal to zero only when both the temperature and density approach to the critical point. When temperature approaches the critical temperature, we will have the expression for the critical isotherm by using Equation (5-22) and for $\rho \to \rho_c$ the Equation (5-23) can describe the critical isochore. Writing the equation of state in this present form allows us to construct more expressions for the equation of state near the critical point, such as

$$\Delta\rho = \Delta\mu \left(t + \Delta\mu^{1/(\gamma+\beta)} \right) \Phi_3 \left(t, \Delta\mu^{1/(\gamma+\beta)} \right) \tag{5-24}$$

and

$$\Delta\rho = t \left(\Delta\mu + t^{\gamma+\beta} \right) \Phi_4 \left(\Delta\mu, t^{\gamma+\beta} \right) \tag{5-25}$$

where Φ_3, Φ_4 are homogeneous functions of their variables with $-(\gamma+1)$ degrees of homogeneity and $\Delta\rho$ is analytic in t and $\Delta\mu$ in the one phase region. Notice that the way we have chosen the fluctuation variables near the critical point t, $\Delta\rho$, and $\Delta\mu$ with proper exponents, such as t, $\Delta\rho^{1/\beta}$, and $\Delta\mu^{\frac{1}{\gamma+\beta}}$, in order to 'scale' all the critical exponents with the right order. Use the same technique in V-3 which we have shown the equivalence between Widom and Griffiths' equation of state near the critical point, we can transform Widom-like expression Equations (5-22, 23, 24, 25) to Griffiths-like expression as follows:

$$\Delta\mu = \Delta\rho \, |\Delta\rho|^{\delta-1} \, h_1(x_1) \tag{5-26}$$

$$\Delta\mu = t^{\gamma+\beta} \, h_2(x_2) \tag{5-27}$$

$$\Delta\rho = \Delta\mu^{1/\delta}\, h_3(x_3) \tag{5-28}$$

$$\Delta\rho = t^{\beta}\, h_4(x_4) \tag{5-29}$$

where $x_1 = t/|\Delta\rho|^{1/\beta}$, $x_2 = |\Delta\rho|/t^{\beta}$, $x_3 = t/\Delta\mu^{1/(\gamma+\beta)}$, $x_4 = \frac{\Delta\mu}{t^{\gamma+\beta}}$

$h_1(x_1) = (1+x_1)\,\Phi_1(x_1, 1)$, $h_2(x_2) = (1+x_2)\,\Phi_2(x_2, 1)$,

$h_3(x_3) = (1+x_3)\,\Phi_3(x_3, 1)$, $h_4(x_4) = (1+x_4)\,\Phi_4(x_4, 1)$.

By assumption, for fixed density is analytic in t, so the function $h(x_1)$ in Equation (5=26) can be expanded in a power series, giving

$$\Delta\mu = \Delta\rho\,|\Delta\rho|^{\delta-1} \sum_{n=0}^{\infty} a_n x_1^{\,n} \tag{5-30}$$

By the same token, we have

$$\Delta\mu = t^{\gamma+\beta} \sum_{n=0}^{\infty} b_n x_2^{\,n} \tag{5-31}$$

$$\Delta\rho = \Delta\mu^{1/\delta} \sum_{n=0}^{\infty} c_n x_3^{\,n} \tag{5-32}$$

$$\Delta\rho = t^{\beta} \sum_{n=0}^{\infty} d_n x_4^{\,n} \tag{5-33}$$

From these equations of state, we are able to describe the thermodynamic behavior near the critical point. We do agree that one should drive all the thermodynamic behavior from one equation of state as Widom and Griffiths have done. However, from a practical point of view, once we have a theoretical model which can describe the critical phenomena with an equation of state like Equation (5-32), one must be able to derive another form like Equation (5-33), and these expressions do offer a clearer

picture than Griffiths' form.

Critical Isotherm (t = 0). We can express the critical isotherm in two ways: from Equation (5-28), we have

$$\Delta\rho = \Delta\mu^{1/\delta}\, h_3(0) \tag{5-34}$$

while from Equation (5-26), we have

$$\Delta\mu = \Delta\rho^{\delta}\, h_1(0) \tag{5-35}$$

Coexistence Curve. Equation (5-29) yields

$$\Delta\rho = t^{\beta}\, h_4(0) \tag{5-36}$$

Critical Isochore. Equation (5-27) gives

$$\Delta\mu = t^{\gamma+\beta}\, h_2(0) \tag{5-37}$$

Compressibility along Critical Isochore. Differentiating Equation (5-27) with respect to density given

$$\partial\mu/\partial\rho)_T = t^{\gamma} h_2'(0) \tag{5-38}$$

Compressibility on the Coexistence Curve. Similar to Equation (5-14), we have

$$\partial\mu/\partial\rho)_T = t^{\gamma}\, \frac{h_1'(-X_{10})}{\beta X_0^{\gamma-1}} \qquad -X_{10} = B^{-1/\beta} \tag{5-39}$$

Specific Heat at Constant Density on the Critical Isochore. The treatment will be the same as V-B. However, we will demonstrate the case using Equation (5-27). The free energy has the following form:

$$A(\rho, T) = A_0(T) + t^{2-\alpha}\, a_2(X_2) \tag{5-40}$$

in the one phase region, with $A_o(T)$ an analytic function of the temperature and $a_3(x_3)$ satisfying the differential equation:

$$a_2'(x_2) = h_2(x) \tag{5-41}$$

By solving the differential equation, we have

$$A(\rho,T) = A_o(T) + t^{2-\alpha}\left(\sum_{n=1}^{\infty} b_{n-1}/n \; X_2^{\,n} + C\right) \tag{5-42}$$

Therefore, the C_V can be obtained:

$$-\frac{C_V}{T} = \frac{\partial^2 A_o}{\partial T^2} + t^{-\alpha}\left\{C' + \sum_{n=1}^{\infty} b_{n-1}\left[\frac{2-\alpha-n\beta}{\beta} - \beta(1-\alpha)(2-\alpha-n\beta)\right]\left(\frac{\Delta\rho}{t^\beta}\right)^n\right\} \tag{5-43}$$

Since $A_o(T)$ is analytic, on the critical isochore, $\Delta\rho = 0$

$$C_V \sim C' t^{-\alpha} \qquad C' = (2-\alpha)(1-\alpha)C$$

(notice that the constant C is the same C derived by Griffiths in Equation (5-19).)

Application and Evidence for the Homogeneous Argument Appeared in the Equation of State for the Theoretical Model

A. Experimental Confirmation

Magnetic Systems. In 1967, Kouvel and Rodbell[40] studied the experimental data for Ni and CrO_2. Although the critical behavior for these two ferromagnets are quantitatively very different, they found both of them obey the same special type of equation of state which is isomorphic with Widom's assumption for the equation of state near the critical point.

A few months later, Arrott and Noakes[41] found that the critical behavior for Ni does agree with the scaling assumption proposed by Griffiths.

Most recently, Ho and Litster[42] have found that the insulating ferromagnet $CrBr_3$ near its critical temperature can be explained by an equation of state with scaling assumption.

Therefore, it is confirmed by these experiments that the scaling assumption for the equation of state near the critical point is a proper criterion for explaining the critical phenomena.

Fluid System. Recently, Vicentini-Missoni, Sengers and Green[43] have proposed an equation of state near the critical point which is based upon Griffiths' scaling assumption. With this empirical equation of state they have found the agreement with various experiments. The proposed equation of state can be expressed as follows:

$$\Delta\mu = \Delta\rho\,|\Delta\rho|^{\delta-1}\,h(x) \qquad (5\text{-}44)$$

$$h(x) = E_1\left(1+x/x_0\right)\left[1+E_2\left(1+x/x_0\right)^{2\beta}\right]^{\frac{[\beta(\delta-1)-1]}{2\beta}}$$

with $\Delta\mu = \mu(\rho,t) - \mu(\rho_c,t)$, $\Delta\rho = (\rho-\rho_c)/\rho_c$

$$t = \frac{T-T_c}{T_c} \quad , \quad x = t/|\Delta\rho|^{1/\beta}$$

E_1 and E_2: adjustable constants and x_o can be determined by the coexistence curve as described by Griffiths.

With x_o, β, δ, E_1, and E_2 as adjustable parameters, they have used a least-square analysis of experimental data and find all the critical exponents and coefficients for CO_2, Xe and He^4. The proposed form of a scaling-law equation doe describe the data of the three gases to within their estimated precision.

B. Theoretical Models

Bragg-Williams Lattice Gas (van der Waals' type gases). From

Equation (3-48), the equation of state for Bragg-Williams lattice gas can be expressed as:

$$P = -J\rho^2 - KT \log(1-\rho) \tag{5-45}$$

The critical point can be determined by $\partial P/\partial \rho)_{T_c} = \partial^2 P/\partial \rho^2)_{T_c} = 0$

$$\rho_c = \frac{1}{2} \quad , \quad KT_c = J/2 \tag{5-46}$$

Following Widom's homogeneous argument we calculate

$$\begin{aligned} \Delta P &= |P - P_c| = |P(\rho, T) - P(\rho_c, T)| \\ &= |-J(\rho^2 - \rho_c^2) - KT[\log(1-\rho) - \log(1-\rho_c)]| \end{aligned} \tag{5-47}$$

By introducing $\Delta\rho = \rho - \rho_c$ and $t = T_c - T$ and using Equation (5-47), we obtain

$$\Delta P = \Delta\rho(t + B\Delta\rho^2 + O(\Delta\rho^3))2K \qquad K = J/KT_c \tag{5-48}$$

By neglecting higher orders of $\Delta\rho$, indeed we get Widom's expression where the homogeneous function Φ is a constant 2K. It is obvious that the isothermal compressibility on the critical isochore

$$\partial P/\partial \rho)_{T, \Delta\rho=0} = \rho^2 K_T \sim t \quad , \text{ i.e. } \gamma = 1$$

is a classical result.

Ideal Bose-Einstein Model. Green and Cooper have utilized the ideal Bose-Einstein model,[44] by introducing a linear coupling of the boson operators to destroy the phase symmetry, to study the physical behavior in the vicinity of the transition. In their analysis the equation of state can be expressed as an ordered series in appropriately

scaled thermodynamic variables. In the vicinity of the transition, the first term in the expansion exhibits the homogeneous form of a scaled equation of state which shows a power-law behavior with non-classical exponents. The equation of state near the critical point was written as:

$$\Delta\mu = \Delta\rho\,|\Delta\rho|^{\delta-1}\,h(x = t\Delta\rho^{-1/2}) \qquad (5\text{-}49)$$

where $$h(x) = (1 + 3/2\,x)^2$$

The complete set of critical exponents is $\alpha = -1$, $\beta = 1/2$, $\gamma = 2$, $\delta = 5$, which satisfies the equalities conjectured by Widon and Fisher.

The Scheme of Kadanoff.[49] In 1966, Kadanoff introduced a model for describing the behavior of the Ising model very near T_c. The description is based upon dividing the Ising model into cells which are microscopically large but smaller than the coherence length and then using the total magnetization within each cell as a collective variable. From this model, he found that the singular part of the free energy per atom, that is, the part yielding the dominant singularities in the thermodynamic functions near the critical point, can be expressed as:

$$A(t,H) = t^{2-\alpha}\,F(t^{\delta\beta}/H) \qquad t>0$$
$$= |t|^{2-\alpha}\,G(|t|^{\delta\beta}/H) \qquad t<0 \qquad (5\text{-}50)$$

There is not explicit expression for F or G; however, with this expression the scaling assumption is satisfied.

The Scheme of Domb and Hunter.[45] Domb and Hunter have used high temperature series expansion to characterize the behavior of the Ising model of a ferromagnet in a non-zero magnetic field. For small values

of field and temperature near T_c, the equation of state is proposed as

$$H = M t^{\gamma} G(M^2 t^{-2\beta}) \tag{5-51}$$

with $$G(u) = \sum_{n=0}^{\infty} B_n u^n \qquad (u = M^2/t^{2\beta})$$

If we replace t^{γ} (which is $t^{\beta(\delta-1)}$) by $|M|^{\delta-1}$ and $u^{-\frac{1}{2}}$ by x, we will have the same expression as Griffiths. There is no exact expression for B_n.

CHAPTER VI

HOMOGENEOUS EQUATION OF STATE FOR LIQUID DROPLET MODEL NEAR THE CRITICAL POINT

From the last chapter we have noticed that the homogeneous equation of state for the critical region has been widely used and confirmed for a variety of gases and magnetic materials. However, only a few theoretical modles have implicitly constructed such a homogeneous equation of state and explicitly expressed the homogeneous function in specific forms. In this chapter the liquid droplet model introduced by Fisher is used to establish a homogeneous equation of state which agrees with the homogeneous argument of the equation of state exactly. At the same time, we carry through the liquid droplet model to quantitatively meaningful answers.

Homogeneous Equation of State for Liquid Droplet Model near the Critical Point[11]

In Chapter IV Fisher's droplet model was shown to give the pressure and density for an infinite system as:

$$P/kT = g_0 \sum_{l=1}^{\infty} l^{-\tau} x^{l\sigma} y^{l} \tag{6-1}$$

and

$$\rho = g_0 \sum_{l=1}^{\infty} l^{1-\tau} x^{l\sigma} y^{l} \tag{6-2}$$

where

$$x = \exp[-a_0(w-\omega T)/kT] \tag{6-3}$$

$$y = \bar{z} \exp(E_0/kT + S_0/k) \tag{6-4}$$

with the assumption that the most probable surface area $\bar{S}$ of a cluster size ℓ will vary as $\simeq a_o \ell^{\sigma}$ ($\ell \to \infty$) with, necessarily for $d \geq 2$, $0 < \sigma < 1$, where $a_o = a_o(T)$, and no interaction between dimensionality clusters. (Notations are defined in Chapter IV.)

From Fisher's analysis, the critical point is located at x = 1, and y = 1, i.e.

$$T_c = W/\omega \quad , \qquad \bar{z}_c = \exp - (E_o/KT + S_o/K) \tag{6-5}$$

and near the critical point,

$$\ln x = - a_o (W - \omega T)/KT = - a_o W (1 - T/T_c)/KT = - (T_c - T)/T_c D \tag{6-6}$$

where $$D = KT/a_o W$$

$$\ln y = \ln \bar{z} - \ln \bar{z}_c = (\mu - \mu_c)/KT \tag{6-7}$$

The critical pressure, density, and compressibility factor (critical ratio) can be written as follows:

$$P_c/KT_c = \delta_o \sum_{\ell=1}^{\infty} \ell^{-T} = \delta_o \zeta(T) \tag{6-8}$$

$$\rho_c = \delta_o \sum_{\ell=1}^{\infty} \ell^{1-T} = \delta_o \zeta(T-1) \tag{6-9}$$

$$P_c/KT_c\rho_c = \zeta(T)/\zeta(T-1) \tag{6-10}$$

where $\zeta(x)$ is a Zeta function of x.

With this information, we start to establish the homogeneous equation of state for liwuid droplet model and its quantitative analysis.

A. Equation of State in the Region $T_c > T$ and $\mu_c > \mu$

In this region, we define $t = (T_c - T)/T_c$ and $\Delta\mu = (\mu_c - \mu)/kT$, and hence from Equations (6-7) and (6-6) we have

$$\ln x = -t/D \tag{6-11}$$

and

$$\ln y = -\Delta\mu \tag{6-12}$$

We first start from Equation (6-2), near the critical point we can approximate Equation (6-2) as

$$\rho = g_0(T-2)\,\zeta(T-1)\int_1^\infty \ell^{1-T} x^{\ell^\sigma} y^\ell \, d\ell \tag{6-13}$$

We replace the sum by an integral with a factor $(T-2)\,\zeta(T-1)$ in order to get agreement with ρ_c at $x = y = 1$.

Use Equations (6-11) and (6-12) $-t = D \ln x$ and $\Delta\mu = -\ln y$, and change variable $\ell = \xi/\Delta\mu$, we have

$$\rho = g_0(T-2)\,\zeta(T-1)\,(\Delta\mu)^{T-2}\int_{\Delta\mu}^\infty \xi^{1-T}\exp(-c\xi^\sigma - \xi)\,d\xi \tag{6-14}$$

where $c = t/D\Delta\mu^\sigma$.

Now we can treat ρ as a function of c and expansion in a Taylor series of c yields

$$\rho(c) = \rho(0) + d\rho/dc\Big)_0 c + \cdots + \frac{c^n}{n!}\, d^n\rho/dc^n\Big)_0 + \cdots \tag{6-15}$$

Now
$$d^n\rho/dc^n = (-1)^n g_0(T-2)\,\zeta(T-1)\,\Delta\mu^{T-2}\int_{\Delta\mu}^\infty \xi^{1-T+n\sigma} e^{-\xi} d\xi$$

$$= (-1)^n g_0(T-2)\zeta(T-1)\,\Delta\mu^{T-2}\,\Gamma(2-T+n\sigma, \Delta\mu) \tag{6-16}$$

where $\Gamma(2-\tau+n\sigma, \Delta\mu)$ is an incomplete Gamma function and can be expressed in terms of the following form:[46]

$$\Gamma(2-\tau+n\sigma, \Delta\mu) = \Gamma(2-\tau+n\sigma) - \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \frac{\Delta\mu^{2-\tau+n\sigma+m}}{2-\tau+n\sigma+m} \qquad n \neq 0$$

$$\Gamma(2-\tau, \Delta\mu) = \left[\Gamma(3-\tau) - \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} \frac{\Delta\mu^{3-\tau+m}}{3-\tau+m} - \Delta\mu^{2-\tau} e^{-\Delta\mu} \right] / 2-\tau$$

$$n = 0 \qquad \Gamma > 2 \qquad (6\text{-}17)$$

By neglecting higher orders of $\Delta\mu$, we have

$$\rho(c) = \sum_{n=0}^{\infty} \frac{(-1)^n}{n!} c^n \delta_0 (\tau-2)\zeta(\tau-1)\Delta\mu^{\tau-2}\Gamma(2-\tau+n\sigma, \Delta\mu)$$

$$= \delta_0 \zeta(\tau-1)\Delta\mu^{\tau-2}\left[\Delta\mu^{2-\tau} - \Gamma(3-\tau) + (\tau-2)\sum_{n=1}^{\infty} \frac{(-1)^n \Gamma(2-\tau+n\sigma)}{n!} c^n\right] \qquad (6\text{-}18)$$

$$= \delta_0 \zeta(\tau-1)\left\{1 - \Delta\mu^{\tau-2}\left[\Gamma(3-\tau) + (\tau-2)\sum_{n=1}^{\infty} \frac{(-1)^{n+1}\Gamma(2-\tau+n\sigma)}{n! D^n} \left(t/\Delta\mu^{\sigma}\right)^n\right]\right\}$$

with $\rho_c = \delta_0 \zeta(\tau-1)$, $\Delta\rho = (\rho_c - \rho)/\rho_c$, and $\delta = 1/(\tau-2)$, $1/\sigma = \delta\beta$

(See Equations (4-58, 61), (6-9), we have

$$\Delta\rho = \Delta\mu^{1/\delta}\left[\Gamma(3-\tau) + (\tau-2)\sum_{n=1}^{\infty}(-1)^{n+1}\frac{\Gamma(2-\tau+n\sigma)}{n! D^n}\left(\frac{t}{\Delta\mu^{1/\delta\beta}}\right)^n\right] \qquad (6\text{-}19)$$

$$= \Delta\mu^{1/\delta}\sum_{n=1}^{\infty} c_n \left(t/\Delta\mu^{1/\delta\beta}\right)^n$$

where $$c_n = (-1)^{n+1}(\tau-2) D^{-n} \frac{\Gamma(2-\tau+n\sigma)}{n!}$$

for $n \neq 0$ (6-20)

$$c_0 = \Gamma(3-\tau)$$

Comparing with Equation (5-32), we see we get exactly the same expression as for the equation of state near the critical point with the scaling assumption.

By using Equations (6-11), (6-12), and (6-13), we also can make the change of variable $\frac{t}{D}\ell^{\sigma} = \xi'$ and have

$$\rho = \beta_0(T-2)\zeta(T-1)D^{\frac{2-T}{\sigma}} t^{\frac{T-2}{\sigma}} \int_{t/D}^{\infty} \xi'^{\frac{2-T-\sigma}{\sigma}} e^{-\xi'} e^{-c'\xi'^{1/\sigma}} d\xi'$$

$$c' = D^{\frac{1}{\sigma}} \Delta\mu / t^{1/\sigma} \qquad (6\text{-}21)$$

Use the same analysis and we can obtain

$$\Delta\rho = t^{\beta}\left[\frac{\Gamma(1-\beta)}{D^{\beta}} + \beta/D^{\beta}\sum_{n=1}^{\infty}(-1)^{n+1}\frac{\Gamma(n-\beta)}{n!}D^{\gamma/\delta\beta}\left(\Delta\mu/t^{\delta\beta}\right)^{n}\right]$$

$$= t^{\beta}\sum_{n=0}^{\infty} d_n\left(\Delta\mu/t^{\delta\beta}\right)^{n} \qquad (6\text{-}22)$$

where $d_n = (-1)^{n+1}\beta D^{n-\beta}\frac{\Gamma(n-\beta)}{n!}$ $\qquad n \neq 0$

$$d_0 = \Gamma(1-\beta)/D^{\beta}$$

which again exactly agrees with Equation (5-33).

B. Equation of State in the Region $T > T_c$ and $\mu < \mu_c$

For this case, we assume $t' = (T - T_c)/T_c$ and $\Delta\mu = (\mu_c - \mu)/kT$ and therefore,

$$\ln x = t/D \qquad \text{and} \qquad \ln y = -\Delta\mu \qquad (6\text{-}23)$$

We notice that the only thing has changed is the sign for ln x. Therefore Equations (6-14) and (6-21) can be written as

$$\rho = \beta_0(T-2)\zeta(T-1)(\Delta\mu)^{T-2}\int_{\Delta\mu}^{\infty}\xi^{1-T}\exp(\bar{c}\xi^{\sigma} - \xi)\,d\xi \qquad (6\text{-}24)$$

where

$$\bar{c} = t'/D\Delta\mu^{\sigma} \qquad (6\text{-}25)$$

where $\bar{c}' = D^{\frac{1}{\sigma}} \Delta\mu / t'^{\frac{1}{\sigma}}$.

From Equation (6-24) we can derive the following form using the same analysis as before:

$$\Delta\rho = \Delta\mu^{1/\delta}\left[\Gamma(3-\tau) - \sum_{n=1}^{\infty}(\tau-2)D^{-n}\frac{\Gamma(2-\tau+n\sigma)}{n!}\left(\frac{t'}{\Delta\mu^{1/\delta\beta}}\right)^n\right]$$
$$= \Delta\mu^{1/\delta}\sum_{n=0}^{\infty} C_n'\left(\frac{t'}{\Delta\mu^{1/\delta\beta}}\right)^n \qquad (6\text{-}26)$$

where $C_n' = -(\tau-2)D^{-n}\,\Gamma(2-\tau+n\sigma)/n! \qquad n \neq 0$

$C_0' = \Gamma(3-\tau)$.

However, for Equation (6-25) we are not allowed to have a power series with a from as: $\Delta\rho = t'^{\beta}\sum_{n=0}^{\infty}\eta_n(\Delta\mu/t'^{\delta\beta})^n$, simply because when $\bar{c}'$ = 0 the density is going to approach infinity. Another way to look at this problem is that the equation of state, Equation (6-1) or (6-2) is not analytic for $x > 1$ (i.e. $\ln x > 0$) at $y = 1$ (i.e. $\Delta\mu = 0$).

C. Equation of State in the Region $T < T_c$ and $\mu > \mu_c$

Use the same argument as we have had in Section B, we cannot have the expression for $\Delta\rho = \Delta\mu'^{1/\delta}\sum_{n=0}^{\infty}\eta'_n\,(t/\Delta\mu'^{1/\delta\beta})^n$

where $\Delta\mu' = (\mu-\mu_c)/KT$, but will have

$$\Delta\rho = t^{\beta}\left[\Gamma(-\beta+1)/D^{\beta} - \beta/D^{\beta}\sum_{n=1}^{\infty}\frac{\Gamma(2n-\beta)}{n!}D^{n/\sigma}\left(\frac{\Delta\mu'}{t^{\delta\beta}}\right)^n\right]$$
$$= t^{\beta}\sum_{n=0}^{\infty} d'_n\left(\frac{\Delta\mu'}{t^{\delta\beta}}\right)^n \qquad (6\text{-}27)$$

where $d_n' = -\beta\, D^{n/\sigma-\beta}\left(\Gamma(n-\beta)/n!\right) \qquad n \neq 0$

$d_0' = \Gamma(1-\beta)/D^{\beta}$

D. Equation of State in the Region $T > T_c$ and $\mu > \mu_c$

In this region, the equation of state does not exist for the droplet model. It is not hard to see that the series in Equation (6-1) is not convergent for $x > 1$ and $y > 1$.

Now we can conclude that the droplet model does give an explicit expression corresponding to the scaling assumption for the equation of state near the critical region. Since all the coefficients in the series contain three parameters τ, σ, and D, all the critical phenomena can be described by these three parameters. The significance of these three parameters will be discussed in the following:

(i) Significance of σ. From the definition of this parameter we can see that σ is a critical parameter describing the shape of the surface of the cluster near the critical point. For example, when the ℓ-cluster is in spherical shape, the corresponding value for σ is 2/3, and for the cluster with all the molecules sitting on the surface the corresponding value will be 1 (or a long chain of molecules).

(ii) Significance of D. From the definition (See Equation 6-6)

we can interpret D as the ratio of the thermal energy near the critical point and the microscopic surface energy. Therefore, when $D \gg 1$, i.e. the thermal energy (or average kinetic energy per particle) is much larger than the microscopic surface energy we will not expect any phase transition. On the other hand we shall expect the magnitude for D near the critical point having the order 1.

(iii) Significance of τ. The significance of seems to be more ambiguous than the other two parameters. In Fisher's paper,[10] the parameter was explained as due to the 'closed' effect on the surface of the cluster

near the critical point and only depending on the dimensionality. We shall review the significance of τ later in this chapter.

Furthermore, we notice that in Equations (6-26), we replace t' by -t, we get Equation (6-20). It is also true that replacing $\Delta\mu'$ by $-\Delta\mu$ in Equation (6-27) yields Equation (6-22). Therefore, near the critical point for the liquid droplet model we have only two expressions with the scaling assumption. In these equations of state the even powers in the series do not vanish which means the liquid droplet model does not provide the symmetric condition as given in Widom and Griffiths' analysis (in which the free energy is an even function of $\Delta\rho$, hence $\Delta\mu$ is an odd function of $\Delta\rho$). Therefore, for further study of the droplet model, we recommend adding a constraint imposing this symmetric condition onto the liquid droplet model. With this condition, we may find a better model for describing the critical phenomena.

Thermodynamic Behavior Near the Critical Point

We have mentioned before that the homogeneous equation of state for the liquid droplet model near the critical point only contains three critical parameters. For this reason, it is obvious that the critical exponents and coefficients must have certain correlations among them. In the last chapter, we noticed that the empirical equation of state proposed by Green et al. has more than five parameters. Therefore it is very significant to find the possible relationship among these critical parameters with physical significance. In this section we try to derive the possible relation among the critical exponents and critical coefficients within the limit of the liquid droplet model.

A. Compressibility Factor at the Critical Point and the Critical Exponent

From Equation (6-10)

$$P_c/kT_c\rho_c = \zeta(\tau)/\zeta(\tau-1) = f(\tau)$$

and $\delta = 1/(\tau - 2)$, there exists a relation between the critical exponent δ and the compressibility factor at the critical point. The idea is straightforward from the liquid droplet model that both quantities are function of τ only. However, it is the first theoretical model has ever suggested this particular relationship. We will carry on the numerical calculation in the next section and propose this relationship to predict experimental results.

B. Critical Isotherm

From the proposed homogeneous equation of state for liquid droplet model near the critical point, Equation (6-19), we can easily determine the critical exponent and coefficient for the critical isotherm, by letting t = 0 we have

$$\begin{aligned} \Delta\rho &= \Delta\mu^{1/\tau-2}\ \Gamma(3-\tau) \\ &= \Delta\mu^{1/\delta}\ \Gamma(1-1/\delta)\ . \end{aligned} \tag{6-28}$$

It is interesting that the critical exponent and coefficient for the critical isotherm only depend on the critical parameter τ. Together with the statement we had in the last section concerning the relationship between δ and the compressibility factor at the critical point, it means whenever we locate the critical point, i.e. determine the critical pressure, density and temperature, with this model, we can predict the behavior for the critical isotherm.

C. Coexistence Curve

With the analysis of the liquid droplet model, we notice that no

real coexistence curve can be found. Since for $\mu_c < \mu$ and $T < T_c$, we only can find the density for the gas part, $\rho < \rho_c$. However, near the critical point when $\mu \to \mu_c$, Equation (6-22) will behave like a coexistence curve,

$$\Delta\rho = t^{\frac{\tau-2}{\sigma}} \Gamma\left(\frac{\sigma+2-\tau}{\sigma}\right) / D^{\tau-2/\sigma}$$
$$= t^{\beta} \Gamma(1-\beta) / D^{\beta} \qquad (6\text{-}29)$$

Again, it is interesting to see the association with the critical parameters that the critical coefficient is much dependent upon the critical exponent.

D. Isothermal Compressibility K_T on the Critical Isochore

We can derive the isothermal compressibility on the critical isochore very easily from Equation (6-22). When we check back to Equation (5-29), we can see the K_T on the critical isochore can be expressed as

$$\rho^{-2} K_T = t^{-\gamma} h_4'(0)$$
$$= t^{-\gamma} d_1$$
$$= t^{-\gamma} \beta D^{\gamma} \Gamma(1-\beta) \qquad (6\text{-}30)$$

We are not able to find the isothermal compressibility on the critical isochore for $T > T_c$, since the pressure, density and compressibility are not analytic in this region, as we have discussed before. It is also not proper to calculate the isothermal compressibility along the coexistence curve because the droplet model does not provide a complete coexistence curve. Therefore it is a worthwhile program for the future to push this

liquid droplet model in a form which can provide all the information near the critical point.

Applications[12]

In this section we will utilize the droplet model to make a quantitative analysis near the critical point. Since the model itself does not provide the calculation for the three critical parameters, we have to use the known experimental data to fix τ, σ, and D and then calculate all the critical exponents and coefficients provided by the droplet model. The results show a striking agreement with the experiment.

A. Compressibility Factor and Critical Exponent

From the last section we found that there is a relationship between the compressibility factor at the critical point and the critical exponent δ. With the known P_c, T_c and ρ_c we are able to calculate the critical exponent δ, or for given δ we can predict the compressibility factor at the critical point.[12]

On this basis, we have investigated the δ for fluids by given compressibility factor at the critical point, and compressibility factor at the critical point for van der Waals' gases, Bragg-Williams' lattice gases and Ising lattice gases by the known δ-value.

From the experimental point of view, it is easier to determine the critical pressure P_c, critical temperature T_c, and critical density ρ_c and hence the compressibility factor at the critical point, then the critical exponent δ. With this in mind, we have chosen the known compressibility factor at the critical point to predict the δ-values for fluids. Three classes of substances, which include simple almost spherical non-polar molecules, most ellipsoidal hydrocarbons, and polar gases

are investigated. For the simple almost spherical non-polar molecules, δ varies from 4.2 to 4.5. As for the hydrocarbons we have examined 17 different substances, which are listed in Table VI-1. The value of δ for this group is approximately equal to 5, except for Ethylene and n-Butane which have the value 4.48 and 5.3 respectively. There are large deviations for the class of polar gases (see Table VI-1). The calculated value of δ ranges from 4.9 to 7.9, however, except for C_2H_5Cl, all of them are larger than 5.0. Comparing these calculated δ-values with the available results obtained by experimental analysis for some non-polar almost psherical gases, we see that the proposed relation is in excellent agreement with experiment (see Table VI-2). Therefore, we have predicted the δ-value is about 5.0 for hydrocarbons and larger then 5.0 for polar molecules.

Both of these quantities are exactly known for van der Waals' gas and Bragg-Williams' lattice gas. Therefore, we can use wither quantity as our input data. Here we used δ =3 and the corresponding compressibility factor at the critical point calculated by the droplet model is 0.392, which is very close to the values obtained by the theoretical models, which have 0.375 and 0.3863 for van der Waals and Bragg-Williams lattice gas respectively (see Table VI-3). For Ising lattice gases, we have checked the square and triangular lattices in two dimensions, and simple cubic and face-centered cubic lattices in three dimensions. In three dimensional Ising lattice gases, the value of is suggested as 5.20 ± 0.15,[8] which will give the compressibility factor at the critical point, from the proposed relation, as 0.252 - 0.2645. Comparing with the results estimated by Ising lattice gases itself, 0.246 for simple cubic

Table VI-1. Calculated Date for the Critical Exponent

Simple Almost Spherical Non-Polar Molecules

Molecule	Compressibility Factor[48]		
He^4	0.305	2.237	4.218
He^3	0.30378	2.235	4.240
H_2	0.302	2.234	4.272
Ne	0.296	2.228	4.383
A	0.291	2.223	4.479
Xe	0.290	2.222	4.499
N_2	0.292	2.224	4.460
O_2	0.292	2.224	4.460
CH_4	0.290	2.222	4.499
CO_2	0.287	2.219	4.558
Hydrocarbons			
Ethane	0.267	2.200	5.000
Propane	0.270	2.203	4.921
Isobutane	0.276	2.209	4.788
n-Butane	0.257	2.191	5.308
Isopentane	0.268	2.201	4.967
n-Pentane	0.266	2.199	5.013
n-Hexane	0.260	2.194	5.156
n-Heptane	0.258	2.192	5.206
n-Octane	0.258	2.192	5.206
Benzene	0.265	2.198	5.037
Cyclohexane	0.276	2.209	4.788

Table VI-1 (Continued)

Molecule	Compressibility Factor		
Diisopropyl	0.266	2.199	5.013
Diisobutyl	0.262	2.196	5.107
Ethyl Ether	0.262	2.196	5.107
Ethylene	0.291	2.223	4.479
Propylene	0.273	2.206	4.854
Acetylene	0.275	2.208	4.810
Polar Molecules			
CH_3CN	0.181	2.126	7.926
H_2O	0.224	2.162	6.177
NH_3	0.238	2.174	5.744
CH_3OH	0.220	2.158	6.311
CH_3CL	0.258	2.192	5.206
C_2H_5Cl	0.269	2.202	4.944

Table VI-2. Available Experimental Analysis of the Critical Exponent

Gases	δ	Reference
CO_2	4.6 ± 0.06	(43)
	4.0**	(49) (50)
Xe	4.6 ± 0.1	(43)
	4.2**	(49) (51)
H_2	4.2**	(49) (52)
He^4	4.45 ± 0.10	(43)

**Larson and Sengers suggested that in the critical region the P-ρ isotherms may in fact be much flatter than has been inferred from PVT work because of inherent limitations in the method. Therefore the values of δ are expected to be larger than the values indicated in the Table with **.

Table VI-3. Comparison of Compressibility Factor at the Critical Point Predicted by the Proposed Relation with Results Obtained by other Theoretical Models

	δ	Model	Prediction
van der Waals	3	0.375	0.392
Bragg-Williams	3	0.3863	0.392
Square Lattice	15	0.0986	0.1018
Triangular Lattice	15	0.1112	0.1018
Simple Cubic Lattice	5.20±0.15	0.246	0.258±0.006
Face-Centered Cubic Lattice	5.20±0.15	0.258	0.285±0.006

lattice and 0.285 for face-centered cubic lattice,[47] the agreement seems reasonable. In tow dimensional Ising lattice gases, it is generally believed that the δ-value is exactly equal to 15 for a variety of lattices.[8] From our calculation, the corresponding compressibility factor at the critical point is 0.1018. Comparing with the value of 0.0986, obtained from Ising model calculation, for square lattice gas we have less than 5% deviations. Comparing with the value of 0.1112 for triangular lattice gas we have less than 10% error. Therefore, the model dependent proposed relation strongly suggests that there is a connection between the critical exponent δ and the compressibility factor at the critical point. At the same time, within the model, the structure dependence of the τ-value, which is generally believed to be a parameter only dependent on dimensionality as we mentioned beofre, may also throw some light on the significance of the critical exponents.

It will be interesting to have some experimental measurements of the critical exponent δ for some substances in the class of hydrocarbons and polar gases to confirm or demonstrate the inadequacies of the proposed formula.

B. Critical Exponents and Coefficients

Here, we have chosen the experimental data of CO_2, Xe, and He^4 to compare with the calculated data obtained from the analysis of the liquid droplet model. As we mentioned before the model itself does not provide values for τ, σ, and D, thus we have to use the epxerimental data to determine these three parameters. We have selected the compressibility factor at the critical point, β and B (determined by the coexistence curve), merely because more complete and reliable information can be

Table VI-4. Notations for Thermodynamic Function for a Fluid Near the Critical Point

Coexistence Curve	$\Delta\rho \simeq B(-t)^{\beta}$	
Heta Capacity at the Constant Volume	$C_v \simeq A/\alpha\,[t^{-\alpha}-1]$	$\alpha>0$
	$\simeq -A \ln t$	$\alpha=0$
Critical Isotherm	$\Delta\mu \simeq \Delta\,(\Delta\rho)^{\delta}$	$t=0$
Isotherm Compressibility	$K_T \simeq c\,t^{-\gamma}$	$t<0$

Table VI-5. Critical Exponents and Coefficients in Terms of Three Parameters Appeared in the Liquid Droplet Model

$$\delta = \frac{1}{\tau - 2} \quad , \quad \beta = \frac{\tau - 2}{\sigma} \quad , \quad \gamma = \frac{3 - \tau}{\sigma}$$

$$\alpha = 2 - \frac{\tau - 1}{\sigma}$$

$$\Delta = \left[\frac{1}{\Gamma(1 - \frac{1}{\delta})} \right]^{\delta}$$

$$B = \Gamma(1-\beta) / D^{\beta}$$

$$C = \Gamma(1-\beta) D^{\gamma} \beta$$

$$\frac{P_c}{K T_c \rho_c} = \frac{\zeta(\tau)}{\zeta(\tau - 1)} \, .$$

Table VI-6. Experimental Data for the Critical Exponents and Coefficients

Gases	α	β	γ	δ	B	C	Δ
CO_2		0.34±0.015	1.35±0.15	5±1	1.83	0.1	1.5
				4.0[49]			1.18±0.1[49]
Xe	0.08[54]	0.35±0.015	$1.3^{+0.1}_{-0.2}$	$4.2^{+0.6}_{-0.3}$	1.8	0.2	0.3
				4.2[49]			1.16±0.11[49]
He^4	0.127[55]	0.353±0.003	1.1±0.1	3.8-4.1[56]	1.4		
		0.3742[55]	1.15[55]				
		0.354±0.010[56]					

Table VI-7. Results Obtained from Fitting the Homogeneous Equation of State

Gases	α	β	γ	δ	B	C	Δ
CO_2	0.04	0.350±0.008	1.26	4.60±0.06	2.0	0.0526	2.6
Xe	0.04	0.350±0.008	1.26	4.60±0.1	1.91	0.059	3.3
He^4	0.05	0.359±0.002	1.24	4.45±0.10	1.44	0.130	3.2

Table VI-8. Fitting Data from the Homogeneous Equation of State for the Liquid Droplet Model

Gases	Compressibility Factor*(17)	α	β^*	γ	δ	C	B^*	Δ	τ	σ	D
CO_2	0.287	0.0546	0.35	1.225	4.558	0.1824	1.83	0.842	2.219	0.6267	0.4505
Xe	0.290	0.0754	0.35	1.245	4.499	0.2278	1.8	0.870	2.222	0.635	0.525
He^4	0.304	0.1267	0.36	1.156	4.218	0.4989	1.4	0.827	2.237	0.660	1.0

*Experimental data used to determine τ, σ, D.

obtained for these than for other critical exponents and coefficients. Notice that we do not choose two critical exponents at the same time. For doing that we can simply calculate the other critical exponents by the equalities of the critical exponents instead of using the analysis of the model. From the last section, by knowing the compressibility factor, we are able to calculate the critical parameter τ. Combining the calculated value of τ and given β we can determine the second parameter. Together with B, which is a function of τ , σ , and D, we can complete the information of these three parameters.

In Table VI-4, we summarize the notations for thermodynamic functions for a fluid near the critical point. Table VI-5 shows the critical exponents and coefficients in terms of three parameters appearing in the liquid droplet model. Table VI-6 gives the experimental data of the critical exponents and coefficients and Table VI-7 gives the results obtained by Vicentini-Missoni, Sengers and Green, from fitting the homogeneous function they proposed. Table VI-8 demonstrates the calculated data from the liquid droplet model and the experimental data used for fixing the undetermined three critical parameters.

Discussion

From our study of the liquid droplet model, it strongly suggests that this model can be considered as a good candidate for describing the critical phenomena. We shall summarize the reasons in the following manner:

1. It has been proved by Fisher that the liquid droplet model can verify Mayer's conjecture for the singularity behavior of the equation of state near the critical point. From the analysis in Cahpter 4, the small-

est real positive singularity does give the condensation point in this model.

2. Fisher also has demonstrated that the critical exponents in the droplet model only depend upon two critical parameters. In other words, the critical exponents in the liquid droplet model do satisfy the equalities for the critical exponents which have been conjectured by Widom and Fisher and confirmed by various experimental results.

3. The liquid droplet model offers an explicit expression for the equation of state near the critical point which exactly agrees with the scaling assumption, which is another important criteria for critical phenomena.

4. The most important of all is that the correlation between the critical exponents and coefficients predicted by the droplet model has been verified by different experimental data for various substances.

Therefore, we can be very certain that the present form for the liquid droplet model can be considered as a good trend for further study of the critical phenomena.

However, we have to be very careful not to draw a conclusion that the liquid droplet model in the present form is THE MODEL for describing the critical phenomena. As we noticed before, plenty of justifications are needed to bring this model in a completely satisfactory presentation for critical phenomena. We shall summarize these again in the following way:

1. The liquid droplet model cannot explain all the regions near the critical point because of the restriction of the analyticity for the equation of state. For example, we are not able to study the critical

isochore in the region of $T > T_c$, and the critical isotherm in the region of $\mu > \mu_c$, etc.

2. The liquid droplet has three undetermined parameters. Comparing with the Ising lattice gases, which provides all the calculations by itself, the liquid droplet model definitely does not offer completely self-consistent information. Therefore, a microscopic picture is needed to construct the detailed information for the physical clusters.

3. The significance of the critical parameter τ is not clear. From Frenkel-Band's droplet model we notice that the corresponding parameter is fixed due to the dynamic part (appeared in the partition function from the momentum space) and from Mayer's theory, the corresponding parameter can be derived simply from the geometric construction (derived from the configuration integral). Fisher merely puts this parameter into his equation of state to fulfill the requirement for describing the critical phenomena. Therefore, physical justification is needed for the significance of the critical parameter τ.

4. In calculations for the compressibility factor at the critical point, we notice that for a given τ, the $\ell = 1$ term gives a significant contribution in the Zeta function sums. Also, when we replace the sum in the equation of state by an integral to get the homogeneous expression for the equation of state near the critical point, we notice that we have a lower cutoff $\ell = 1$. Both in turn means the cluster which only contains a single molecule is very important near the critical point. Therefore, droplet model has been extended far beyond the region where physical intuition provides some justification.

With these analyses we conclude that, even though, as claimed by

Uhlenbeck, the critical phenomena is common to all substances, one would expect it to be possible to give a very general explanation demanding no exact knowledge of the detail interaction between molecules, there is still no theoretical model can provide such general theory for the critical phenomena. However, with all the evidences we have discussed, we do think the liquid droplet model can be a starting point for the study of this 'simple' common phenomenon.

APPENDIX

APPENDIX A. Legendre Transformation[15]

Let us consider a function $y = y(x)$ (A-1)

with its derivative $p = dy/dx$ (A-2)

or $dy = p\,dx$. (A-3)

We define the Legendre transformation of $y(x)$ as

$$\psi(p) = px - y(x) \tag{A-4}$$

We assume that Equation (A-2) can be solved for $x = x(p)$ which is possible if

$$d^2y/dx^2 \neq 0. \tag{A-5}$$

Thus x can be eliminated from the right-hand side of Equation (A-4). This relation can also be put in the form

$$\psi(p) = x\,dy/dx - y = x^2\,d(y/x)/dx \tag{A-6}$$

The equivalence of $\psi = \psi(p)$ with Equation (A-1) is evident from the fact that the latter can be regained from the former. The relation is dual in the sense that the inverse and direct relations have the same form. Indeed, we have from Equation (A-4)

$$d\psi = x\,dp + p\,dx - dy = x\,dp \tag{A-7}$$

and hence

$$x = d\psi/dp. \tag{A-8}$$

This equation can be solved for $p = p(x)$ provided

$$d^2\psi/dp^2 \neq 0 \tag{A-9}$$

Therefore p can be eliminated from

$$y = px - \psi = p^2\,d(\psi/p)/dp \tag{A-10}$$

and we recover Equation (A-1). Thus in the domain where the conditions

(A-5) and (A-9) are satisfied the transformation y, $x \leftrightarrow \psi$, p is information-preserving and entirely symmetric.

APPENDIX B. The Energy Minimum Principle for Different Representations due to Legendre Transformation[15]

Helmholtz potential (F = U - TS) Minimum Principle. The equilibrium value of any unconstrained internal parameter in a system in diathermal contact with a heat reservoir minimizes the Helmholtz potential at constant temperature (equal to that of the heat reservoir).

Enthalpy (H = U + PV) Minimum Principle. The equivalent value of any unconstrained internal parameter in a system in contact with a pressure reservoir minimizes the enthapy at constant pressure (equal to that of the pressure reservoir).

Gibbs Function (G = U - TS + PV) Minimum Principle. The equivalent value of any unconstrained internal parameter in a system in contact with a temperature and a pressure reservoir minimizes the Gibbs function at constant temperature and pressure (equal to those of respective reservoirs).

BIBLIOGRAPHY*

1. G. E. Uhlenbeck, Critical Phenomena, N. B. S. Misc. Publ. No. 273, Eds. M. S. Green and J. V. Sengers (Washington: National Bureau of Standards), p. 3, 1966.

2. J. D. van der Waals, Dissertation, 1873.

3. M. Kac, G. E. Uhlenbeck and P. C. Hemmer, J. Math. Phys. 4, 216, (1963).

4. A. V. Voronel', V. G. Snigirev, and Yu. R. Chashkin, Soviet Physics-JETP 21, 653, (1965).

5. M. E. Fisher, J. Math. Phys. 5, 944, (1964).

6. C. N. Yang and T. D. Lee, Phys. Rev. 87, 404, (1952).

7. T. D. Lee and C. N. Yang, Phys. Rev. 87, 410, (1952).

8. Critical Phenomena, N.B.S. Misc. Publ. No. 273, Eds. M. S. Green and J. V. Sengers (Washington: National Bureau of Standards), 1966; M. E. Fisher, Rept. Progr. Phys. 30, part II, pp 731-826; Kadanoff, L. P., et al., Rev. Mod. Phys. 39, 396, (1967).

9. B. Widom, J. Chem. Phys. 43, 3898 (1965).
R. B. Griffiths, Phys. Rev. 158, 176 (1967); L. P. Kadanoff, Physics 2, 293 (1966)

10. M. E. Fisher, Physics 3, 255 (1967).

11. C. S. Kiang, Bull. Am. Phys. Soc., 14, 847 (1969), Atlanta University Center Science Research Institute Research Report No. 14, 1969.

12. C. S. Kiang, Bull. Am. Phys. Soc., 14, 835 (1969); Bull. Am. Phys. Soc., 15 91 (1970); Phys. Rev. Letters, 24, 47, (1970); Z. Physik, in press, (1970).

13. L. Tisza, Generalized Thermodynamics, The M.I.T. Press, Cambridge, Massachusetts, (1966).

14. L. Tisza, Ann. Phys. (N.Y.), 13, 1-92, (1961).

15. H. B. Callen, Thermodynamics, John Wiley and Sons, Inc., New York, (1960).

16. L. D. Landau and E. M. Lifshitz, Statistical Physics, Pergamon Press, Ltd., London, 1958.

* All abreviations in this bibliography are adopted from Physics Abstracts.

17. K. Huang, Statistical Mechanics, John Wiley and Sons, Inc., New York, (1963).

18. L. Van Hove, Physica 15, 951 (1949).

19. A. F. Andreev, Soviet Physics-JETP, 18, 1415 (1964); M. E. Fisher, Proc. Centennial Conference on Phase Transition, University of Kentucky, 1965 (unpublished), ref. 10.

20. G. S. Rushbrooke, J. Chem. Phys., 39, 842, (1963).

21. R. B. Griffiths, Phys. Rev. Letters 14, 623, (1965); J. Chem. Phys. 43, 1958, (1965).

22. B. Widom, J. Chem. Phys., 37, 2703, (1962).

23. M. E. Fisher, J. Chem. Phys. 38, 802, (1963).

24. L. Onsager, Phys. Rev. 65, 117, (1944).

25. G. E. Uhlenbeck, P. C. Hemmer, and M. Kac, J. Math. Phys. 4,(1963); P. E. Hemmer, M. Kac, and G. E. Uhlenbeck, J. Math. Phys. 5,(1965).

26. J. Lebowitz and O. Penrose, J. Math. Phys. 5, 841 (1964); J. Math. Phys., 7, 98, (1966).

27. T. Burke, J. Lebowitz, and E. Lieb, Phys. Rev., 149, 118 (1966).

28. E. Ising, Z. Phys. 31, 253, (1925).

29. L. Onsager, Nuovo Cimento Suppl. 6, 261, (1949); C. N. Yang, Phys. Rev. 85, 808, (1952); see also E. W. Montroll, R. B. Potts and J. C. Ward, J. Math Phys., 4, 308, (1963).

30. Review article by C. Domb, Advanced Physics 9, Nos. 34, 35, (1960).

31. Review article by G. A. Baker, Jr., Advances in Theoretical Physics I, Ed. K. A. Brueckner, New York: Academic Press (1965).

32. T. Matsubara and H. Matsuda, Progr. Theor. Phys (Japan) 16, 416, 569, (1956).

33. B. Kahn, Dissertation University of Utrecht, North-Holland Publishing Co., Amsterdam, 1938; Studies in Statistical Mechanics, Vol. 3, 201, (1965).

34. J. E. Mayer, and S. F. Harrison, J. Chem. Phys., 6, 87, (1938); J. E. Mayer, J. Chem. Phys. 10, 629, (1942); Ibid., 15, 187, (1947); J. E. Mayer and M. G. Mayer, Statistical Mechanics, John Wiley and Sons, New York, (1949).

35. J. Frenkel, J. Chem. Phys. 7, 200, 538 (1939); Kinetic Theory of Liquids, Oxford University Press, London, (1946).

36. W. Band, J. Chem. Phys. 7, 324, 927 (1939).

37. S. Katsura, Advances in Physics, 12, 391, (1963).

38. T. L. Hill, Statistical Mechanics, McGraw-Hill Book Company, Inc. New York, (1956); R. H. Fowler, Statistical Mechanics, Cambridge University Press, (1936).

39. O. K. Rice, Statistical Mechanics, Thermodynamics and Kinetics, W. H. Freeman and Company, San Francisco and London, (1967).

40. J. S. Kouvel and D. S. Rodbell, Phys. Rev. Letters, 18, 215 (1967), 20, 1237 (1968).

41. A. Avrott and J. E. Noakes, Phys. Rev. Letters, 19, 786 (1967).

42. J. T. Ho and J. D. Litster, Phys. Rev. Letters 22, 603 (1969).

43. M. Vicentini-Missoni, J. M. H. Levelt Sengers and M. S. Green, Phys. Rev. Letters 18, 1113 (1967), 22, 389 (1969).

44. M. J. Cooper and M. S. Green, Phys. Rev. 176, 302 (1968).

45. C. Domb and D. L. Hunter, Proc. Phys. Soc. (London) 86, 1147 (1965).

46. Higher Transcendental Functions, based on notes left by H. Bateman, McGraw-Hill, New York (1953).

47. M. E. Fisher, Phys. Rev. 136, A1599 (1964).

48. J. O. Hirschfelder, C. F. Curtiss and R. B. Bird, Molecular Theory of Gases and Liquids, John Wiley and Sons, Inc., New York (1964).

49. B. Widom and O. K. Rice, J. Chem. Phys. 23, 1250 (1955).

50. A. Michels, B. Blaisse, and C. Michels, Proc. Soc. (London), Ser. A 160, 358 (1937).

51. H. W. Habgood and W. G. Schneidered, Can. J. Chem. 32, 98, 164 (1954).

52. H. L. Johnston, K. F. Keller, and A. S. Friedman, J. Am. Chem. Soc. 76, 1482, (1954).

53. M. E. Fisher, Phys. Rev. 136, A1599 (1954).

54. C. Edwards, J. A. Lipa, and M. J. Buckingham, Phys. Rev. Letters 20, 496 (1968).

55. M. R. Moldover, Phys. Rev. 182, 342 (1969).

56. P. R. Roach, Phys. Rev. 170, 213 (1968).

VITA

Chia Szu Kiang was born in Shanghai, China on September 9, 1941. He is the son of Kung Mei Kiang and Hui Ching Kiang.

He first attended public school in Chung Ching, China, at the age of three and was publicized by his family as a "wonder child." He was graduated with the highest honors from Chieh Kou High School in June, 1957, at Taipei, Taiwan. He attended National Taiwan University from September, 1957 to June, 1961, when he received the degree of Bachelor of Science in Physics. From June, 1961 to September, 1962, he served in the National Chinese Army. In September, 1962, he left his native country and attended Georgia Institute of Technology to pursue a graduate program in Physics. He received the degree of Master of Science in Physics from the Georgia Institute of Technology in March, 1964. In 1965, he was found to be a tuberculosis patient. With the help from Dr. and Mrs. V. Crawford and with intensive care from the Battey State Hospital, Rome, Georgia, he recovered from T.B. and discovered a new attitude towards life. From that time until he married Marilyn Maisel in February, 1968, he was a "wandering hippy" searching for his own life. The marriage brought him back to the "normal" society. With the patience and understanding of his advisor, Dr. H. A. Gersch, he is able to pursue the union-card for higher education, namely, the degree of Doctor of Philosophy in Physics.

From September, 1967 to the present date, he has been employed by Clark College Physics Department as an assistant professor. He is a member of the American Physical Society and numerous honorary societies.